THE BASIS OF MODERN ATOMIC THEORY

BY

C. H. DOUGLAS CLARK

B.SC. HONS. (LOND.), D.I.C.

ASSISTANT LECTURER IN CHEMISTRY, UNIVERSITY OF LEEDS

1627
4-NOV 1927
COIMBATORE

WITH FORTY-FOUR DIAGRAMS

METHUEN & CO. LTD.

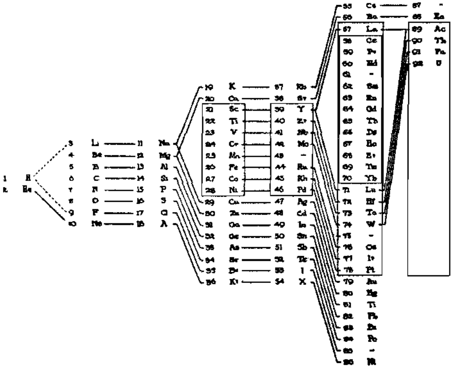
36 ESSEX STREET W.C.

LONDON

TABLE I

A PERIODIC CLASSIFICATION OF THE ELEMENTS

(*Nature*, 1923; **112**, 30)



The lines connect elements having similar properties. Elements enclosed within rectangles also tend to resemble each other. Explanation is given in Section 50 (p. 205).

First Published in 1926

PRINTED IN GREAT BRITAIN

PREFACE

THE purpose of this volume is to provide a clear account of the general experimental and logical basis of recent atomic theories. Conversations with students prove that many who are familiar with atomic models fail to appreciate the experimental background, but that, when explanations are offered, no difficulty exists in arousing interest. Some time ago, the author read a paper entitled "Atoms" before a Society composed mainly of students, and the measure of success which, in spite of difficulties, attended this effort, encouraged him to believe that something further might be attempted with advantage. The result is embodied in the present work, where very little previous knowledge is assumed. The argument goes back to Dalton's theory, from which point the subject is carefully reasoned, the relevant experimental work being quoted at each step. Attention has been specially paid to certain points which, though evidently essential to the argument, appear to have been insufficiently emphasised hitherto.

An attempt is made to attain logical completeness, and it therefore becomes necessary to cover a large amount of ground. It appears desirable, for instance, to treat the "quantum" theory in some detail before proceeding to discuss "quantized" electronic orbits. When so much work is under review, considerable difficulty is experienced in doing justice to all workers in the different fields. Some of the conclusions given could have been equally well deduced from evidence other than that here selected.

The subject-matter has been presented concisely, sometimes in the form of tables, largely with the object of restricting the cost of production. Certain conclusions are stated without proof, where the steps in the argument leading to them can be very readily supplied. In such cases, the reader is especially urged not to proceed until he has satisfied himself in regard to the particular point.

Diagrams have been used to illustrate the text, and it is suggested that the construction of models may be found helpful, as a means of overcoming the difficulty of thinking in three dimensions of space.

A large number of selected references to the original literature are given in lists at the ends of the chapters. The titles of the papers are stated in full, and each reference has been checked. It is hoped that these lists, while encouraging students generally to read the original memoirs, will be found useful to those engaged in research, to teachers and other more advanced workers. Suggestions as to desirable inclusions will be gratefully received by the author.

The order of development is, in general, not the historical one, since it frequently happens that a result is most satisfactorily considered in the light of subsequent researches.

The argument is mainly non-mathematical. Bohr's theory of circular orbits in hydrogen and singly ionized helium, however, after being treated in a purely qualitative way, is later developed quantitatively from the standpoint of angular momentum. The basis of the mechanical principles assumed will be found in standard works on applied mathematics. A considerable number of formulæ are introduced throughout the book without proof, and a list of the symbols used is provided for reference.

The original treatises have been the main source of information, though the author is also much indebted to contemporary works, especially those mentioned in the bibliographical list at the end of the volume. These works will be found useful to those who wish to follow any part of the subject in greater detail.

The author has been particularly fortunate in securing the assistance of colleagues. Dr. E. C. Stoner has very kindly read the entire MS., and by his interest and advice has rendered most valuable service. Mr. J. C. Gregory, B.Sc., has also read through the typescript, and has made helpful suggestions in regard to modes of expression. Professor S. Brodetsky kindly criticised some of the later paragraphs, and Dr. S. H. C. Briggs has offered valuable suggestions in connection with the work arising out of the Lewis atomic model. The author's best thanks are due to the above-mentioned, and to other specialists in different branches who have read portions and given freely of their knowledge and experience, as well as to his brother, Mr. W. E. Noël Clark, B.A., who has executed the drawings for the diagrams.

C. H. D. C.

THE UNIVERSITY OF LEEDS
December, 1925

TABLE OF CONTENTS

	PAGE
PREFACE	vii
LIST OF TABLES	xv
LIST OF FIGURES	xvi
LIST OF SYMBOLS	xvii
LIST OF ABBREVIATIONS USED IN REFERENCES	xix

CHAPTER I

THE ATOM

1. The Atomic Theory	1
2. The Molecular Theory	3
3. The Kinetic Theory	5
4. Evidences of the Existence of Molecules	8
5. The Absolute Mass of Atoms	13
6. The Speeds and Sizes of Molecules	15
7. The Periodic System of the Elements	17
References: (I)	18

CHAPTER II

THE ELECTRON

8. The Ionic Theory of Solutions	21
9. The Charge of an Electron	24
10. The Mass of the Electron	36
11. The Speeds and Sizes of Electrons	37
References: (II)	39

CHAPTER III

ELECTRICITY IN GASES

12. The Mechanism of Gaseous Conduction	41
13. The Discharge at Low Pressures	49
14. Cathode Rays	50
15. Positive Rays	53
16. Mass Spectra and Isotopes	55
17. X-Rays and the Elucidation of Crystal Structure	58
References: (III)	76

PAGE

CHAPTER IV

Radioactivity

18. The Nature of Radioactive Change 81
19. Radioactive Equilibrium 85
20. The Alpha Rays 87
21. The Scattering of Alpha Rays 90
22. The Beta and Delta Rays 93
23. The Gamma Rays 95
References: (IV) 96

CHAPTER V

The Electronic Constitution of Atoms

24. The Emission of Electrons from Matter 100
25. Atomic Numbers 102
26. Secondary X-Rays and Nuclear Charge 103
27 High Frequency Spectra of the Elements 106
28. The Size of the Nucleus 109
29. Isotopes and Isobares 111
30. Influences of the Nucleus upon Atomic Properties 115
31. Radioactive Elements and the Periodic Law 118
References: (V) 120

CHAPTER VI

Radiant Energy

2. The Forms of Radiant Energy 124
3. Electric and Magnetic Induction 126
4. Isothermal Radiation 130
5. Specific Heats at Low and High Temperatures 136
6. The Photoelectric Effect 143
7. Photochemistry and Reaction Mechanism 147
8. Quantum Theory and Nuclear Size 150
9. Difficulties of the Quantum Theory 151
References: (VI) 153

CHAPTER VII

Atomic Architecture: (1) The Nucleus

The Fundamental Problem 157
Constituent Parts of Nuclei 158
Energy Levels in Radioactive Nuclei 162
The Structure of Atomic Nuclei 165
References: (VII) 166

CHAPTER VIII

Atomic Architecture: (2) The Extranuclear Electrons of Isolated Atoms

Levels of the Extranuclear Electrons 168
The Nature of Optical Series Spectra 171
The Bohr Theory of Line Spectra for One Electron . . . 175

PAGE

47. Absolute Magnitudes relating to Circular Orbits 186
48. Elliptic Orbits 189
49. Critical Potentials and Absorption Edges 201
50. Bohr's General Theory of Atomic Structure 205
References: (VIII) 210

CHAPTER IX

ATOMIC ARCHITECTURE: (3) THE EXTRANUCLEAR ELECTRONS IN COMBINATION

51. General Principles 212
52. The Theory of Langmuir 222
53. Intramolecular Ionization 232
54. Theories of Acidity and Alternating Polarities 238
55. Co-ordination Compounds 246
56. Magnetic Theories: Concluding Considerations . . . 256
References: (IX) 264

CHAPTER X

THE PRESENT OUTLOOK

57. The Theory of Relativity 269
58. Limits of Applicability of Calculus and Thermodynamics . . 272
59. Theories of Matter, Energy, and the Æther 274
60. The Outlook for the Future 276
References: (X) 279
BIBLIOGRAPHICAL LIST 281
INDEX OF AUTHORS 283
INDEX OF SUBJECTS 287

LIST OF TABLES

Table No.		Page
I.	A Periodic Classification of the Elements	*Frontispiece*
II.	Magnitudes relating to Atoms and Electrons	38
III.	The Isotopes of Neon	116
IV.	The Isobares of Argon and Calcium	116
V.	Example of the Displacement Law	119
VI.	Limits of Wave-Length for different forms of Energy	126
VII.	Comparison of Properties of Lead and Diamond	143
VIII.	Fundamental Constants of Hydrogen Series Spectra	173
IX.	Fundamental Constants of Ionized Helium Series Spectra	173
X.	Innermost Orbital Data (Hydrogen) and Related Constants	189
XI.	Relative Magnitudes relating to Circular and Elliptic Orbits	197
XII.	Electronic Orbits in Inert Gas Group	208
XIII.	Groups of Ionized and Non-ionized Molecules	213
XIV.	Properties of Polar and Non-polar Molecules	213
XV.	Stabilities of the Hydrides of the Elements	219
XVI.	Comparison of Physical Properties of Nitrogen and Carbon Monoxide	226
XVII.	Structures of various Ions (Langmuir)	230
XVIII.	Structures of some Oxy-acids, showing Mixed bonds	236
XIX.	Dissociation Constants of Halogenated Acids at 25° C.	241
XX.	Effective Atomic Numbers of Complex Platinum Compounds	252
XXI.	Outermost Orbital Electrons of Atoms in Co-ordination Compounds	253
XXII.	Bohr Magneton Numbers (Sommerfeld)	258

LIST OF FIGURES

FIGURE NO. PAGE

I. Slit Ultramicroscope 10
II. Apparatus for Determination of Electronic Charge (Townsend) 26
III. Apparatus for Determination of Electronic Charge (H. A. Wilson) 28
IV. Apparatus for Determination of Electronic Charge (Millikan) 35
V. Apparatus for Ionic Mobility Determination (Rutherford) . 43
VI. Time-Charge Curve (Langevin) 45
VII. Experiment on Cathode Rays (Thomson) 52
VIII. Mass-Spectrograph (Aston) 57
IX. Haüy's Theory (1782) 60
X. Crystal Lattices of the Cubic System 61
XI. Spot-Photograph of Zinc Blende 62
XII. Apparatus for Crystal Structure (W. H. and W. L. Bragg) . 63
XIII. Reflection of X-rays by a Crystal 65
XIV. Some Cubic Structures 67
XV. Structure of Diamond 71
XVI. Apparatus for Radioactive Rays (Rutherford) . . . 83
XVII. Photographs of Alpha Ray Tracks (C. T. R. Wilson) . . 91
XVIII. Apparatus for High Frequency Spectra (Moseley) . . 107
XIX. Energy—Wave Length—Temperature Curves . . . 133
XX. Specific Heat—Temperature Curve (Hydrogen) . . . 139
XXI. Specific Heat—Temperature Curves (Solids) . . . 142
XXII. Apparatus for Passage of Alpha Rays through Matter (Rutherford) 160
XXIII. Circular Orbits in Hydrogen (Bohr) 176
XXIV. Electron in Elliptic Orbit 191
XXV. Quantized Elliptic Orbits 194
XXVI. Orbital Precession 199
XXVII. Ionization, Absorption and Resonance 202
XXVIII. Atomic Energy Levels 204
XXIX. Polar Combination—Lithium Fluoride (Lewis) . . . 216
XXX. Non-polar Combination. I. Fluorine Molecule (Lewis) . 217
XXXI. Non-polar Combination. II. Oxygen Molecule (Lewis) . 217
XXXII. Tetrahedral Arrangement of Electrons (Lewis) . . . 218
XXXIII. Groups of Varying Stability (Kossel) 219
XXXIV. Nitrogen Molecule (Kossel) 220
XXXV. Twisted Cube Atom (Thomson) 222
XXXVI. Structure of Acetic Acid (Langmuir) 225
XXXVII. Structure of N_2, CO and CN^- (Langmuir) 226
XXXVIII. Structure of CO_2, and N_2O (Langmuir) 227
XXXIX. Diagrammatic Representation of CO_2 Molecule (Langmuir) . 228
XL. Curve of Atomic Diameters (W. L. Bragg) 231
XLI. Ionization of Hydrochloric Acid 240
XLII. Ionization of Ammonia 240
XLIII. Paramagnetic and Diamagnetic Coupling (Oxley) . . . 259
XLIV. Cassinian Ovals 261

LIST OF SYMBOLS

Symbol

- a (1) Constant for X-ray line (Moseley); (2) Major axis of ellipse; (3) No. of links where one electron supplied to an atom.
- A Unit of angular momentum ($= h/2\pi$).
- b (1) Nearest distance of approach of an α-particle to a nucleus; (2) Shielding constant (Moseley); (3) Minor axis of ellipse; (4) No. of links where two electrons are supplied to an atom.
- c (1) Velocity of light in vacuo; (2) No. of electrons added to an atom on ionisation.
- C_v Atomic heat at constant volume.
- d (1) Distance between crystal planes; (2) Molecular diameter.
- D Diffusion coefficient.
- e (1) Electronic charge, or charge on particle; (2) Base of natural logarithms.
- E (1) Charge on hydrogen ion in solution; (2) Energy of radiation and of molecules; (3) Energy of electron in an orbit; (4) No. of shell electrons; (5) No. of electrons in an atomic nucleus.
- f Acceleration of electron.
- F (1) Force acting on a molecule or electron; (2) No. of degrees of freedom.
- g Acceleration due to gravity.
- G Mean velocity of molecules of gas.
- h Planck's constant.
- H Strength of magnetic field.
- I Moment of inertia.
- j Inner quantum number.
- J Potential energy.
- k (1) Radioactive constant; (2) Reaction velocity; (3) Azimuthal (subsidiary) quantum number; (4) Constant equal to R/N (page 132).
- K (1) Total kinetic energy of gas; (2) Intensity of radiation; (3) Ratio pressure to density of a gas.
- l Latus rectum of ellipse.
- L Mean free path of gas molecule or ion.
- m Mass of electron, molecule, or any particle.
- M (1) Mass of nucleus; (2) Unit magneton.
- n (1) No. of molecules in unit volume of gas; (2) Total quantum number; (3) No. of completed octets in a molecule; (4) Number giving order of X-ray spectrum.
- n_r Radial quantum number.
- N (1) Avogadro number; (2) Frequency of revolution.

Symbol	
p	No. of duplets in atomic structures.
P	(1) Pressure of gas; (2) Work done in removing electron from an atom; (3) No. of protons in an atomic nucleus.
q	A constant, equal to Rhc (p. 184)
Q	(1) Energy absorbed by gram molecule of gas; (2) Quantity of electricity; (3) Constant for X-ray series (Moseley).
r	Radius of particle or circular path.
R	(1) Gas Constant; (2) Rydberg constant.
s	Arrhenius constant (reaction velocity).
S	Molecular specific heat.
t	(1) Thickness of sheet; (2) Time interval.
T	(1) Absolute temperature; (2) Kinetic energy of electron.
u	(1) Ionic mobility; (2) Total energy of solid.
u_x	Velocity of ion under field strength X.
U	Total kinetic energy of gas.
U_x	Kinetic energy of motion along x-axis.
v	Velocity of electron, molecule, or other particle.
V	(1) Volume of gas; (2) Potential difference.
V_∞	Ionisation potential.
w	Wave number of spectral line.
W	Energy of electron in an orbit, with sign reversed.
x	A constant, equal to $h\nu/kT$ (p. 141).
x, x_t	No. of radioactive atoms present at times o and t.
X	Strength of electric field.
y	Period of average life of radioactive element.
Y	Total number of particles.
z	Effective atomic number.
Z	Moseley atomic number.
x, y	Rectangular co-ordinates.
r, θ	Polar co-ordinates.
A, B, C, a, β, k	Constants.
ϵ	(1) Energy quantum; (2) Eccentricity of ellipse.
η	Viscosity coefficient.
λ	Wave-length of radiation.
ν	Frequency of radiation.
ν_∞	Limiting frequency of spectral series.
ρ	(1) Density of medium; (2) Number of α-particles deflected through angle greater than given angle.
σ	Density of particle.
τ	Time of half change of radioactive substance.
ω	Angular velocity.

LIST OF ABBREVIATIONS USED IN REFERENCES

Amer. J. Sci.	American Journal of Science.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Astrophys. J.	Astrophysical Journal.
Ber. Deut. Phys. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Brit. Ass. Rep.	Report of the British Association.
Chem. and Ind.	Chemistry and Industry.
Chem. Ber.	Berichte der Deutschen chemischen Gesellschaft.
Chem. News.	Chemical News.
Chem. Zentr.	Chemisches Zentrallblatt.
Compt. Rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
Jahr. Rad. Elekt.	Jahrbuch der Radioaktivität und Elektronik.
J. Chem. Soc., Trans.	Journal of the Chemical Society.
J. Chem. Soc., Proc.	Proceedings of the Chemical Society.
J. Physique.	Journal de Physique et le Radium.
J. Prakt. Chem.	Journal für praktische Chemie.
Naturwiss.	Die Naturwissenschaften.
Phil. Mag.	Philosophical Magazine (London, Edinburgh, and Dublin).
Phil Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Rev.	Physical Review.
Phys. Z	Physikalische Zeitschrift.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Phys Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Sitzungsber. P. Akad. Wiss. Berl.	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Trans., Farad. Soc.	Transactions of the Faraday Society.
Trans. Roy. Dub. Soc.	Transactions of the Royal Society of Dublin.
Verh. Deut. Phys. Ges.	Verhandlungen der Deutschen physikalischen Gesellschaft.
Wied. Ann.	Wiedermann's Annalen.
Z. Anorg. Chem.	Zeitscrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Physik.	Zeitschrift für Physik.
Z. Phys. Chem.	Zeitschrift für physikalische Chemie, Stöichiometrie und Verwandschaftslehre.

"If one link of an argument breaks, the whole drops to the ground; but one step towards an analysis holds good and has an independent value, though we should never be able to make a second. The results which have been obtained by analytical chemistry are not the less valuable, though it should be discovered that all which we now call simple substances are really compounds. All other things are at any rate compounded of those elements: whether the elements themselves admit of decomposition, is an important inquiry, but does not affect the certainty of science up to that point."—J. S. MILL, Introduction to "A System of Logic," 1843.

THE BASIS OF MODERN ATOMIC THEORY

CHAPTER I

THE ATOM

1. The Atomic Theory

THE history of the atomic theory of matter provides an excellent illustration of the power of the experimental method in dealing with old problems, and in preparing the way for new discoveries. The speculations of the early philosophers relating to atoms, such as those of the Roman poet Lucretius, are of historical interest only and proved to be almost perfectly sterile: they were matters of opinion, they rested upon no secure foundation, and led to no developments. The world had to wait many centuries before experimental methods were introduced and laboratory technique became sufficiently improved to be brought to bear upon the problem. In 1662, Boyle, who himself held corpuscular theories of matter, showed by experiment that the density of a gas varied directly as its pressure. Some seventy years later, Bernouilli deduced Boyle's result theoretically on the assumption that a gas contained particles in rectilinear motion. Newton also thought of matter as consisting of atoms. To Dalton, however, undeniably belongs the credit of work which for the first time provided a direct basis for this ancient view of matter.

It appears that several converging lines of evidence led Dalton, during the first decade of the nineteenth century, to publish the theory which bears his name.[1] It is clear that he possessed wide knowledge and great perseverance. His studies included most of the branches of science known in his day. He pointed out, in "A New System of Chemical Philosophy," that the

well-known existence of a substance such as water in three states, solid, liquid, and gas, had tacitly led chemists and physicists to the conclusion that "all bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction, which is more or less powerful according to circumstances." Thus steam was regarded as a more dispersed state of water particles than liquid water, which, in its turn, had less cohesion than ice. It was, however, from experiments on the solubility of gases in liquids that Dalton appears first to have derived direct evidence in favour of this view. He noted that each gas had a characteristic solubility in water, at a given pressure and temperature, but that this varied within wide limits in passing from one gas to another. On the other hand, he was specially struck, in common with his friend and colleague Henry, by the considerable influence of the pressure of a gas upon its absorption in a liquid. An increase of pressure increased the capacity of a liquid to dissolve a gas, and it seemed to him that this fact must be accounted for by particles of gas being forced to a greater extent between particles of the liquid. Now, since the time of Boyle (1661), a distinction had been drawn between "elements," which were made up of one kind of matter only, and "compounds," which were composed of two or more elements. Dalton made the definite suggestion that any one element was composed of a large number of small atoms all of which were alike for the same element and possessed the characteristic properties of the element. Unfortunately, however, he also spoke of the "atom" of a compound; this led to some confusion of thought. It would have been more consistent had he always used, as he sometimes did, the terms "elementary particle" and "compound particle" for the smallest units of element and compound respectively.

It was in another field, however, that Dalton found his atomic theory of special use and importance. He had conducted analysis of ordinary air by the somewhat crude methods available. In one instance, he measured the contraction in volume when air was allowed to react with nitrous gas (nitric oxide) over water. He concluded that a fixed amount of oxygen in the air could unite with a certain fixed amount of nitrous gas or with twice this amount, but not with intermediate quantities. He also found simple relationships when two elements combined to form more than one compound, and embodied these results in the familiar "Law of Multiple Proportions." Further, the

conception that a definite compound had always fixed composition was at this time struggling for recognition in the face of considerable controversy. Dalton realized that both these generalizations were at once explained if compounds were formed by the union of atoms. Each ultimate particle of a given compound would consist of an identical group of elementary atoms, and the compound would have fixed composition. Extending this principle, one atom of oxygen would unite with either one or two " atoms " of nitric oxide, but no intermediate compound would be possible. The same reasoning would apply to any reaction, and would thus lead to the Law of Multiple Proportions.

The contributions of Dalton to this subject did not stop at this point. It soon became clear to him that if the numbers of atoms entering into a given combination were known, then analysis of the compound formed should lead to a determination of the relative weights of the atoms themselves. Thus, one part of hydrogen united with about seven parts of oxygen by weight to form water, so that, if combination took place between one atom of oxygen and one of hydrogen, this process being repeated many millions of times, an atom of oxygen should be seven times as heavy as one of hydrogen. The difficulty lay in deciding the numbers of atoms present in a given compound, and Dalton's assumption in the present instance has proved to be incorrect. The value of the fundamental idea introduced must not, however, be underrated on this account.

The atomic theory is still an essential deductive aid. Unfortunately, Dalton did not distinguish between the atom and the molecule of an element. His theory has also required three other corrections. According to modern views, all atoms are composed of protons and electrons, so that the atoms of one element are not fundamentally different from those of another, as Dalton thought, nor are they, as he supposed, indivisible. The discovery of " isotopes " has deposed his postulate that the atoms of any single element are all necessarily identical. Yet his conclusions were for the most part justified by the evidence before him, and have proved to possess an enduring value.

2. The Molecular Theory

Shortly after the announcement of the Atomic Theory, Gay Lussac published his results on the very simple relationships existing between the volumes of gases or vapours taking

part in a chemical reaction and the volumes of those produced by it.[2] This work, as is well known, led to such difficulties that Dalton was inclined to reject it as inaccurate, and it was due to the hypothesis of Avogadro that it became reconciled with the atomic theory.[3] This hypothesis was founded on the assumption that the ultimate particles of elementary gases were not necessarily atoms, but " molecules constituantes " containing one or more of them, and stated that the same volumes of different gases, if measured under the same conditions, contained the same numbers of molecules (1811). It was left to Cannizaro, some fifty years later, to direct attention to the value of this assumption as an explanation of the weight and volume relationships in gas reactions, and as a means by which the numbers of atoms in the molecules of elements and compounds could be ascertained.[4] It was shown that the hydrogen molecule must contain at least two atoms, and that the formula of water was expressed by H_2O and not by HO as assumed by Dalton. Thus, if eight grams of oxygen united with one gram of hydrogen to form water, the atom of oxygen would be eight times as heavy as two atoms of hydrogen, or sixteen times as heavy as one. Using Avogadro's hypothesis, measurements of the densities of these gases led to the same conclusion. Many atomic weights thus determined were so nearly whole numbers that Prout advanced the suggestion that all the atomic weights of the elements referred to hydrogen would be found integral by more accurate measurement. Later work led to the abandonment of this attractive hypothesis, and it was found convenient to take $O = 16$ as the standard, on which scale hydrogen becomes 1·008, according to the very precise estimations of Morley.[5] Since the discovery of isotopes, however (see section 29) atomic weights have received a somewhat different interpretation, and it would seem that Prout's guess came nearer to the truth than his contemporaries realized.

It follows from Avogadro's hypothesis that the molecular weights of gases are directly proportional to their densities, and that the molecular weight of any gas occupies a fixed volume under standard conditions of temperature and pressure. This volume in C.G.S. units at 0° C. and 760 mm. pressure is 22·42 litres, and may be obtained by dividing the molecular weight of any gas by its density. The number of molecules in this volume is called the Avogadro Number, and is usually denoted by N. There are N molecules in a molecular weight in grams of any substance (apart from association or dissociation),

and similarly N atoms in a "gram-atom"; therefore, division of the ordinary relative atomic weights by N should yield the absolute weights of the atoms concerned in terms of the gram (section 5).

3. The Kinetic Theory

As long as the molecules of matter are considered to be at rest, no ready explanation appears to exist of many observed phenomena, such as those of diffusion and evaporation. Bernouilli had suggested that the particles of a gas were in constant motion in straight lines, and in continual collision with each other and the walls of the containing vessel. By such an assumption, the pressure exerted by gases and their property of filling the greatest possible space became more easily understood. Moreover, the temperature of a gas was connected with the average kinetic energy of movement. Now the diffusion and evaporation of liquids, the vapour tension of solids, and the diffusion of metals into one another [6] tend to show that this hypothesis cannot be limited to matter in the gaseous state. In liquids and solids, however, the movement must be supposed to be more restricted.

A brief reference has already been made to the success of the kinetic theory of gases in deriving Boyle's Law. It also leads to Charles' Law for the proportionality between the volume and the absolute temperature of a gas at constant pressure, as well as to Avogadro's hypothesis. A basis is thus provided for the general gas equation $PV = nRT$, where P, V, and T are the pressure, volume and absolute temperature, and n and R are the number of gram-molecules of gas and the gas constant respectively.

In the realm of chemistry, the kinetic theory of matter has supplied an explanation of the "Law of Mass Action" of Guldberg and Waage, which states that the quantity of chemical action which takes place in a given instance is proportional to the concentrations of the reacting substances.[7] If it is supposed that interaction between two substances is directly dependent upon the frequency of collisions between their molecules, the law follows in this instance quite easily, and may be extended to reactions of higher order. (It may be noted in passing that it is more difficult to account for "monomolecular" reactions, where collision cannot play a direct part, although such cases conform to the general law. The radiation hypothesis of

chemical reaction has been used to give an explanation of the results.[8] The accumulation of energy in certain molecules has also been suggested.[9] On the other hand, some doubt has been thrown on the possibility of occurrence of a true monomolecular reaction.[10] It has been suggested that examples usually assigned to this group may be of a higher order by interaction with impurities.)

It may be useful at this point to consider the kind of picture which has been drawn of the nature of a gaseous system. It is imagined by Planck to be in a state " elementarungeordnet," or of elementary chaos, with unregulated, confused, and whirring intermingling of very many particles. Moreover, the velocities and directions of movement of the molecules of a gas are assumed to be distributed sufficiently at random to justify the use of calculations involving the idea of probability. Maxwell considered the problem of the distribution of velocities among the molecules, assuming that for individual molecules, any given direction of movement and velocity is as likely as any other. The number of molecules being very great, the probability increases that the whole should appear to behave according to a defined law, in spite of the irregularities of individual particles. Maxwell derived an expression corresponding to the " Law of Errors," which gives, for instance, the probable distribution of shots on a target by practised marksmen.[11] Further and improved proofs of the law were given later by Boltzmann and Pirogoff. A little consideration shows that the most probable state of a system will be the most disordered, and the disorder or the *entropy* of a system always tends to increase. Boltzmann, in fact, showed that the entropy of any system is measured quite simply by the logarithm of the probability of the state occurring.

The above example has been cited as a case of probability or statistical calculation in physics. By such reasoning, Planck accounted for the distribution of energy between the various wave-lengths radiated by a " black " body (section 34); by similar reasoning again, Boltzmann deduced the " Equipartition Law." This law has been discussed in the present connection, and therefore perhaps deserves some reference.

Applied to gases, the Equipartition Law may for the present purpose be stated in the simple form that each " degree of freedom," or independent kind of movement, is associated with the same amount of kinetic energy. The atom of a monatomic gas may be regarded as having three degrees of freedom, for it can

move in each of the three directions at right angles to each other independently. No other kind of movement, such as rotation, is here postulated. This matter will be given further attention in section 35. A diatomic gas has a greater number of degrees of freedom, and is regarded as capable of rotation as well as translation. Now the conception of absolute temperature as the average *kinetic energy of molecules is embodied in a fundamental relation* $U_x = \frac{1}{2}RT$, where U_x is the kinetic energy associated with motion parallel to a given x-axis for one gram-molecule of a gas. This energy then corresponds to that of one degree of freedom, and the total energy of a gas may be obtained by multiplying by the number of such degrees. Thus for a monatomic gas, $U = \frac{3}{2}RT$. This relation has been accurately verified by Pier up to 2350° C., in the case of argon.

An interesting development from the point of view of chemical theory is the deduction of Dulong and Petit's Law, which states that the atomic heat (atomic weight multiplied by specific heat) of any element is constant, and equal to about 6·4. In a solid, the atoms are considered as vibrating in simple harmonic motion. There is potential energy as well as kinetic energy, and the average energies of each kind for a complete swing are equal to each other. This virtually has the effect of doubling the number of degrees of freedom, making six in all. This makes $U = 3RT$. Using the approximate value $R = 2$ calories, when $T = 1$, $\Delta U = 6$ calories per degree. This will be equal to the specific heat at constant volume, and when converted to specific heat at constant pressure agrees very nearly with the empirical value of Dulong and Petit. This was regarded as a triumph for the kinetic theory of gases. As is well known, however, there are many notable exceptions to the law, which will occupy attention in considering the quantum theory (section 35).

The apparent conflict between the postulated perpetual movement of the molecules and Carnot's thermodynamical principle will be discussed in section 58.

The kinetic theory of matter is useful, because it visualizes processes. It does not appear to conflict with any experimental evidence. On the other hand, it fails to explain some observations, so that some further hypothesis seems to be necessary (see Chapter VI).

4. Evidence for the Existence of Molecules

The kinetic hypothesis has been confirmed by many researches since the time when it was proposed. Among these, the three following are important: the phenomena connected with Crookes' "radiometer," the observations of Smoluchowski, concerning the condition of a gas near the point of liquefaction, and the evidence supplied by the Brownian movement.

The radiometer consists of a delicate paddle wheel having vanes made of a non-conductor of heat, usually mica.[12] One face of each vane is blackened, the other being silvered. The whole is enclosed in an exhausted glass bulb. On exposure to heat the paddle rotates, moving as though the black surfaces were repelled by the radiation. Now, if the motion were due to a real "radiation pressure," as it is called, the direction of rotation should be the opposite of that observed, for a bright surface reflects the radiation and therefore effects a change of energy twice as great as that produced by a black surface, whic merely absorbs it. A satisfactory explanation is given by th kinetic theory. Because it absorbs the radiation, the blackene surface rises in temperature, while the silvered surface does no and the residual gas in the bulb in contact with the blackene surface is therefore slightly warmer. But this rise of tempera ture implies greater kinetic energy and, therefore, increase velocity of the gas molecules, and the molecular impacts agains the blackened surface will be correspondingly more violen The blackened surface will thus experience a pressure, and wi move away from the radiation. It is clear that this evidenc may be interpreted in favour of the existence of molecules.

It should be mentioned that at rather higher pressures convection currents completely mask this true molecular effect and cause the wheel to move in the opposite direction, while a exceptionally high vacuum and with very delicate apparatu the true radiation pressure can be observed.

With reference to Smoluchowski's contribution to this sub ject, it has been observed that the kinetic theory of gases in th hands of Maxwell involved the conception of a definite distribu tion of velocities among the molecules. Thus, although a given average velocity is directly connected with the temperature o a gas, individual molecules vary on each side of the mean value Evidence of this might be obtained by observations conducted on a gas very near its liquefying point, for, if certain portions of the gas are actually at slightly lower temperatures than

others, local liquefaction might possibly be detected. When this effect was observed, Smoluchowski deduced from it an uneven distribution of temperature, and a corresponding variation of molecular velocity.[13] The formation of a cloud intermediate between the gaseous and liquid states had, as is well known, been previously observed by Andrews.[14]

The most convincing evidence of the existence of molecules in movement, however, is probably supplied by the Brownian movement. In the year 1827, the botanist Brown observed that very small particles of solid or bubbles of gas suspended in a liquid were subject to peculiar vibratory movements, which appeared to be spontaneous, and to continue without ceasing for indefinite periods. The cause of these movements of small particles appears to have been first assigned to the impacts of molecules upon them by Carbonelle, some fifty years later. This view has gradually gained acceptance. It was supported by Bodoszewski, Ramsay, and Gouy,[15] and developed to the point of proof by Perrin, de Broglie, Millikan, and other workers.

The fine suspensions of solid substances in liquids known as "colloidal" solutions have received a considerable amount of attention, particularly in more recent times. By means of the ultramicroscope, described at the close of the year 1902 by Siedentopf and Zsigmondy, it has been found possible to study the movements of these tiny particles in detail.[16] In principle, this instrument depends upon the observation of Tyndall, that a colloidal solution appears milky when viewed at right angles to the direction of the incident light.[17] This is due to scattering of the light by the colloidal particles, and, if examined under a microscope set at right angles to the incident light, the particles appear as luminous points in continuous, irregular motion, such as would be expected on the kinetic theory. Smoke examined in the same manner shows precisely similar behaviour, but the movements of the particles are much more evident, and may be seen with a very low magnification. The kinetic theory applied to gases and liquids appears to be capable, to this extent, of ocular demonstration. The arrangement of the slit ultramicroscope is shown in Fig. 1.

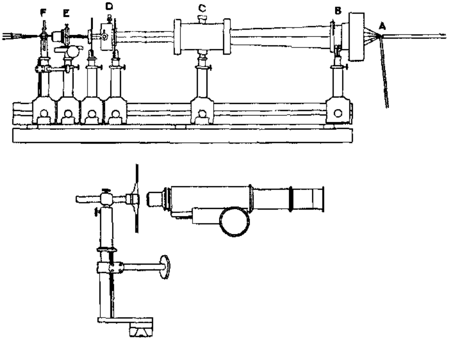
The chief importance of the ultramicroscope, however, lies in the fact that a single particle can be kept continuously in focus, its movements being determined by means of a "network micrometer" inserted in the eyepiece. This consists of a small piece of ruled glass by which the field of view is divided into squares, so that the "co-ordinates" of a given particle can,

with practice, be determined at a given instant. Further, it is possible to find the number of particles in a given volume of solution with the assistance, if practicable, of a photographic attachment by which the particles can be counted at leisure.

Figure I

SLIT ULTRAMICROSCOPE

(*Proc. Roy. Soc.*, 1923; A 102, 603)



A. Source of light—Electric arc.
B. Parabolic condensing lens.
C. Water cell for removing heat rays from beam of light.
D. Crossed slit, adjustable in length and breadth by micrometer screws.
E. Projection objective.
F. *Observation cell, viewed at right angles to the beam through a microscope, as shown in the lower part of the figure.*

The total weight of colloidal substance may be obtained by evaporating down a given volume, and weighing the residue. From the weight of a known number of particles, the average weight of a particle may be obtained. If, further, it is assumed that the density of the colloidal substance is the same in solution

as in bulk, and that the particles are spherical, then their average radius can be estimated. For, from the weight and density combined, the average volume occupied by a particle can be calculated, and hence the radius of a sphere of this volume. The mean of a large number of observations must be taken.

An exact kinetic theory of the displacement of molecules in a viscous fluid medium was first developed by Einstein and Smoluchowski independently in 1905.[18] Einstein considered the trajectory of a single molecule along a definite direction in a given time, and was able to show that the square of the displacement Δx should be proportional to the time t, according to the following relation :—

$$(\Delta x)^2 = \frac{2RTv}{NF}t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which R is the familiar "gas constant," T the absolute temperature, N the Avogadro number, and F the force producing a velocity v of the molecule. The ratio v/F will depend upon the viscosity of the medium. If, now, we apply Stokes' Law, which gives the value of F in terms of the radius r of the particle and the viscosity η of the medium, which may be written as follows,

$$F = 6\pi\eta r v \quad . \quad . \quad . \quad . \quad (2)$$

then, from (1) and (2), eliminating F and v,

$$(\Delta x)^2 = \frac{RT}{3\pi\eta r N}t \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which was the original form of Einstein's equation. This result should, therefore, hold good for particles which obey Stokes' Law. Now, molecules do not do so, though colloidal particles, having radii down to about 5×10^{-4} cms. have been found to give satisfactory agreement. Applied to the fall of particles under gravity,

$$m = \frac{4}{3}\pi r^3(\sigma - \rho) \quad . \quad . \quad . \quad (4)$$

where m is the mass of the particle, and σ, ρ the densities of the particle and medium respectively; from (2) and (4), since $F = mg$,

$$v = \frac{2}{9} \cdot \frac{gr^2}{\eta}(\sigma - \rho) \quad . \quad . \quad . \quad (5)$$

Cunningham has improved this relation by means of a correction factor (p. 33).[19] The equation is simplified if ρ can be neglected in comparison with σ.

The mean displacement of colloidal particles in a given time can be measured by ultramicroscopic methods, and hence the applicability of equation (3) to such cases can be tested, if N, η and T are known, the value of r being obtained from equation (5).

The relation between the value of Δx and the viscosity was investigated by Svedberg, who caused a colloidal solution to flow at a measured speed through the observation chamber of an ultramicroscope.[20] The particles traced out paths resembling sine curves, and the amplitude of vibration was found to vary with the viscosity in the manner indicated by Einstein. A little later, Seddig investigated the influence of temperature upon the amplitudes, and fairly good agreement with Einstein's equation was observed.[21] The experimental values were actually 6 per cent. higher than those given by the equation, the deviation being attributed to a constant error in the measurement of temperature. Further, Perrin tested the relationship indirectly, using suspensions in liquids, and obtained a value of N in general conformity with values obtained by independent methods.[22] In similar fashion, de Broglie examined its validity for drops of water condensed upon small charged particles of tobacco smoke.[23] He applied an electric field, and measured the velocity of movement of the particles. By this means, he was able to test equation (1) above, which does not assume the truth of Stokes' Law. Using Perrin's value of N, he obtained a value of the charge on the particle in general agreement with the accepted value of the electronic charge (see next chapter). The force F here equals the strength of the field multiplied by the charge on the particle, hence the determination of F by means of equation (1) leads to a measurement of the latter charge. De Broglie also found that the mean Brownian displacement in gases at pressures down to 1 cm. of mercury was independent of the pressure.[24] This independence is demanded by the equation. The work of de Broglie was the first evidence that Einstein's relation held good for particles in gaseous as well as liquid media. The accurate work carried out by Fletcher [25] and others has further substantiated this conclusion.

Now Einstein's equation is applicable to molecular movement, and, since a large amount of evidence indicates that it is satisfied by the displacements of colloidal particles, it is diffi-

cult to avoid the conclusion that molecules also conform to it. Molecules must, then, really exist, and must be in constant motion, as the kinetic theory had long postulated. This work at any rate convinced Ostwald that experimental evidence had been found of "the discrete or grained nature of matter for which the atomic hypothesis sought in vain for hundreds and thousands of years." He adds: "The atomic hypothesis is thus raised to the position of a scientifically well-founded theory" (Ostwald's "Outlines of Chemistry").

Zsigmondy has detected particles having a radius of about 4×10^{-6} mm., while the chemical molecule, according to recent evidence, has a radius of the order 0·1 to 1×10^{-6} mm. The scattering of light produced by particles which are between 4 and 40 times as large as the chemical molecule has thus been observed. Scherrer has more recently claimed to have detected, using X-rays, particles of colloidal gold smaller than can be observed in the ultramicroscope.[28]

5. The Absolute Mass of Atoms

The determination of the Avogadro number N in recent times is an event of great significance. It is defined as the number of molecules in a gram-molecule of a substance, and from it the number in a c.cm. of gas can easily be obtained. During the last century, estimates were made of N based on somewhat uncertain computations of the average radius of a molecule of air. In Meyer's "Kinetische Theorie der Gase," the number of molecules in a c.cm. of air was given as 6×10^{19}, a value a little more than twice as great as that at present accepted. It has been observed that if N is known, the absolute mass of a hydrogen atom can be calculated, or, vice versa, knowing the latter, N is determined. It was stated in the previous section that a value of N has been obtained by applying the equation of Einstein there given to the Brownian movement. An independent method used by Perrin is here considered.[27]

It is well known that the atmosphere becomes less dense further from the surface of the earth. It has been found that the diminution in pressure of a column of gas conforms to the two following laws :—

(1) In passing through the same vertical distance, no matter where it is taken in the column, the ratio between the pressures at the two ends of the measured distance is constant. This

involves, if we consider a series of levels ascending in regular steps, that the pressures at these levels will decrease in geometrical progression.[28]

(2) In two different gases, the heights which correspond to a given relative diminution in pressure are inversely proportional to the weights of the molecules of the gases. Thus the height through which it is necessary to pass in the case of hydrogen is sixteen times as great as that in oxygen for the pressure to be reduced by the same fraction in each case.

Perrin conceived the idea of using the colloidal solution of a resin, counting the numbers of particles at different levels in order to obtain a value of N. He first centrifuged the particles to make them as far as possible of uniform size. They were observed directly by means of a microscope, which was focussed on a given level near the surface, and the number of particles in the field of view counted. This number gave a measure of the concentration at the level, and Perrin thus determined the ratios of concentration at different levels, by moving the microscope through known distances. It appeared from these experiments that the above-mentioned laws were obeyed. Now the distance it is necessary to rise in hydrogen for the concentration to be halved is known by experiment. Perrin, therefore, measured as accurately as possible the small distance passed through in the colloidal solution for the concentration to be halved, and thus, knowing the weight of the colloidal particle, deduced, by Law (2) above, the absolute weight of a hydrogen molecule. From this, the value of the Avogadro number was derived. Perrin varied the conditions of experiment as much as possible, and also used other independent methods, and obtained satisfactory agreement. The mass of a hydrogen atom, obtained by halving that of the molecule, came to be $1{\cdot}4 \times 10^{-24}$ gram, the value of N being about 70×10^{22}.[29] The weights of other atoms can be derived from that of hydrogen, using the ordinary relative atomic weights.

The Avogadro number can also be derived from other experimental results, of which the following may be noted: determinations of the viscosity of gases, observations of the spectrum of radiation inside an isothermal enclosure, measurement of the electronic charge and the energy emitted by radioactive substances. The best value of N may be taken to be $60{\cdot}6 \times 10^{22}$. Considering the diversity of the methods employed, and the general agreement between them, this important constant has been measured with remarkable accuracy in spite of great

experimental difficulty. Millikan claims that the error in his value of $N = 60{\cdot}62 \times 10^{22}$ is not greater than 1 in 1000.

It thus appears that Perrin's original value was somewhat too high. A fairly considerable error may have been introduced by the assumption that the density of the colloidal particles of resin was identical with that of the resin in bulk, whereas it is actually somewhat different. This density was used in calculating the weight of the colloidal particle. Further, it is clear that the particles must have varied in size and weight.

It has been pointed out by Burton [30] and by Porter [31] that the distribution of particles in colloidal solution is uniform as a whole. Perrin found a gradation because he worked extremely near the surface of the liquid.

6. The Speeds and Sizes of Molecules

Considerations based on the kinetic theory of gases have enabled determinations of the velocities and diameters of molecules to be made.

The molecules of a gas at a given temperature do not move with equal speeds. It is clear that any tendency to equality in speed would be counteracted by the continual random encounters, by which the velocities and directions of movement must, in general, be altered. Maxwell's Law was the result of his consideration of the problem of the probable distribution of velocities among the molecules. The kinetic theory, however, postulates that the temperature of a gas depends directly upon the average kinetic energy of the molecules. Moreover, since there are the same number of molecules n in unit volume of all gases under the same conditions (Avogadro), it follows that this volume of any gas has the same total kinetic energy K at a given absolute temperature T. Since kinetic energy depends upon the mass of the molecule m as well as its velocity G, it follows that molecules of different gases have different average speeds at the same temperature. These facts are expressed, according to elementary kinetic theory of gases, by the relationship :—

$$P = \frac{1}{3}nmG^2 = \frac{2}{3}K \qquad . \quad . \quad . \quad (6)$$

It can be seen at once that P must be proportional to K, since

both P and K are proportional to the absolute temperature T, for a given number of molecules of gas. From (6), we have—

$$G^2 = \frac{3P}{nm} = \frac{3P}{\rho} \quad . \quad . \quad . \quad (7)$$

since the density ρ of a gas equals nm, by definition. This method of obtaining G was first used by Joule, and subsequently by Clausius for the calculation of the mean molecular speeds of gases. The velocity of a hydrogen molecule at 0° C. has been computed to be 1·8 kilometres per second. That of the heavier oxygen molecule is less, being about 0·4 kilometre per second, and that of the relatively very heavy mercury atom in the vapour of mercury is 0·17 kilometre per second. The order of the velocity of a molecule of air is that of a rifle bullet. These speeds are, however, not so great that the effect of gravity upon them is negligible, or the earth would lose its atmosphere.

Turning next to the question of the sizes of molecules, it has been stated that Zsigmondy used the ultramicroscope to detect colloidal particles of size about $4\mu\mu$ (4×10^{-6} mm.), so that the chemical molecule must at any rate be smaller than this. When the diameter of an atom is discussed, a difficulty is encountered which will be more easily understood when the later chapters of this book have been read. As a matter of fact, the evidence will be seen to support the view that an atom is a highly disperse structure, somewhat resembling that of the solar system. If atoms are assumed to be spherical, then atomic diameter may be conveniently defined as the distance between the centres of two like atoms at the moment of impact.

Various methods have been usefully employed to determine the sizes of atoms and molecules, of which it is proposed to consider here only that based on the measurement of the viscosities of gases. This depends, in the first place, upon Maxwell's equation connecting viscosity with the " mean free path " of a gas. The latter term must be taken to signify the average distance a molecule of gas must travel before it strikes another. The mean free path of a gas is the connecting link between viscosity measurements and the diameters of molecules. Maxwell's relation may be written—

$$\eta = \frac{1}{3}\rho G L \quad . \quad . \quad . \quad . \quad (8)$$

where η is the " coefficient of viscosity " of a gas, L the mean

free path, and ρ and G are, respectively, the density of the gas and mean speed of its molecules. The viscosity of a gas can be measured by rotating a disc in it at known speed, and determining the torsion effect on another disc placed parallel to the first, at a known distance from it.

Clausius, in a pioneer investigation, deduced the other relation required for the present purpose, namely, the relation between the mean free path L of a gas and the molecular diameter d. It is evident that the mean free path must bear some relation to the diameter of the molecule; it will be greater with smaller molecules, and vice versa. Maxwell also calculated the value of L on the basis of his formula for the distribution of velocities among the molecules. As Clausius assumed, for the purpose of calculation, that all the molecules move with a single mean velocity G, Maxwell's result is here given :—

$$L = \frac{1}{\sqrt{2}n\pi d^2} \quad . \quad . \quad . \quad . \quad (9)$$

where n is the number of molecules in unit volume of gas, a number which can be calculated from the known Avogadro number N. Combining equations (8) and (9), L can be eliminated, and d determined in terms of known quantities. The diameter of a hydrogen atom appears to be of the order of 10^{-8} cm. In the case of helium, since the molecule is identical with the atom, the above method gives the diameter of the atom directly as 2×10^{-8} cm. Perrin suggests that such an atom would be lost in a human body almost as completely as the latter would be lost in the volume of the sun!

Another method of calculation of atomic and molecular size, based on the behaviour of X-rays in relation to crystals, will be mentioned in section 17, where reference is also made to Adam's work on the sizes of organic molecules. The different methods of determination of the sizes of atoms and molecules have led to results of the same order of magnitude.

It has been impossible here to do more than outline in non-mathematical fashion those ideas which underlie determinations of the masses, sizes, and velocities of atoms. For further treatment, the original papers must be consulted.

7. The Periodic System of the Elements

It has long been known that when the elements are written out in a list in the order of ascending atomic weights, certain

periodic regularities and similarities are observed. If the elements of the helium group are included in the scheme, then there is generally a resemblance between the properties of a given element and that occurring in the eighth position after it in the list. By writing similar elements beneath each other, groups of elements which show a regular progression in characteristic valency are obtained. Thus the helium group has valency 0, having no inclination to form compounds. The following group, commencing with lithium and sodium are univalent; the next, of which beryllium and magnesium are the first two members, are found to be divalent, and so on through the periodic groups. The periodicity is marked in other ways, such as the gradual development of acid character in passing from group to group, or of basic character in passing from the top to the bottom of a group. There are, however, many irregularities and difficulties, which will appear more fully at later stages. For the present purpose, the arrangement adopted by Bohr is given (Table 1, *Frontispiece*). The elements are numbered successively in order, these numbers being, in fact, the same as Moseley's atomic numbers (section 27, p. 106).

In deciding the internal arrangement of an atom, the regularities exhibited by the periodic system must play an important part. Elements which resemble each other must possess similarity of structure. A theory of atomic structure must also account for the general progression of valency in passing from group to group. It is only within recent times that sufficient evidence has been accumulated to warrant the beginnings of a theory of this kind. In the following pages, this evidence will be presented, and it will be shown to lead to conclusions as to the nature of that systematic inward arrangement of the atom which is so strongly suggested by the regularities of the periodic classification of the elements.

REFERENCES: (I)

See No. 12 in Bibliographical List at end of book

1 (p. 1) "Foundations of the Atomic Theory"; *Alembic Club Reprints*, No. 2. (Simpkin, Marshall, Hamilton, Kent and Co., Ltd., London.) See also H. DEBUS: "The Genesis of Dalton's Atomic Theory"; *Phil. Mag.*, 1896; (vi.) 42, 350.

2 (p. 4) J. L. GAY LUSSAC: "Sur la combinaison des substances gazeuses, les unes avec les autres"; *Mémoires de Physique et de Chimie, Soc. d'Arcueil*, 1808; 2, 207.

3 (p. 4) "Foundations of the Molecular Theory"; *Alembic Club Reprints*, No. 4.

4 (p. 4) S. CANNIZARO: "Considerations on Some Points of the Theoretic Teaching of Chemistry"; *J. Chem. Soc., Trans.*, 1872; **25**, 941.

5 (p. 4) E. W. MORLEY: "The Volumetric Composition of Water"; *Amer. J. Sci.*, 1891; **41**, 220, 276.

Idem: "Ueber die Dichten von Sauerstoff und Wasserstoff und über das Verhältnis ihrer Atomgewichte"; *Z. Phys. Chem.*, 1896; **20**, 68, 242, 417. (Translated from *Smithsonian Contributions to Knowledge*, 1895; **29**.)

6 (p. 5) W. C. ROBERTS-AUSTEN: "On the Diffusion of Metals"; *Phil. Trans.*, 1896; **A187**, 383.

7 (p. 5) C. M. GULDBERG and P. WAAGE: "Ueber die chemische Affinität"; *J. Prakt. Chem.*, 1879; **19**, 69 (abstracted *J. Chem. Soc.*, 1879; **36**, 580).

8 (p. 6) J. PERRIN: "Radiation and Chemistry"; *Trans. Farad. Soc.*, 1922; **17**, 546.

9 (p. 6) J. J. THOMSON: "Recombination of Gaseous Ions, the Chemical Combination of Gases, and Monomolecular Reactions"; *Phil. Mag.*, 1924; **47**, 337.

10 (p. 6) T. M. LOWRY: "Is a true Monomolecular Action Possible?"; *Trans. Farad. Soc.*, 1922; **17**, 596.

11 (p. 6) J. C. MAXWELL: "On the Dynamical Evidence for the Molecular Constitution of Bodies"; *J. Chem. Soc. Trans.*, 1875; **28**, 493.

Idem: "On the Dynamical Theory of Gases"; *Brit. Ass. Rep.*, 1859; 9.

12 (p. 8) W. CROOKES: "On Repulsion resulting from Radiation"; *Phil. Trans.*, 1876; **166**, 325: 1878; **169**, 243: 1879; **170**, 87.

13 (p. 9) VON SMOLUCHOWSKI: "Molekular-kinetische Theorie der Opaleszenz von Gasen im kritischen Zustande, sowie einiger verwandter Erscheinungen"; *Ann. Physik*, 1908; (iv.) **25**, 205.

14 (p. 9) T. ANDREWS: "On the Continuity of the Gaseous and Liquid States of Matter"; *Phil. Trans.*, 1869; **159**, 575.

15 (p. 9) GOUY: "Note sur le mouvement brownien"; *J. Physique*, 1888; (ii.) **7**, 561.

16 (p. 9) H. SIEDENTOPF and R. ZSIGMONDY: "Uber Sichtbarmachung und Grössenbestimmung ultramikroskopischer Teilchen, mit besonderer Anwendung auf Goldrubingläser"; *Ann. Physik*, 1903; (iv.) **10**, 1.

17 (p. 9) J. TYNDALL: "On the Action of Rays of high Refrangibility upon Gaseous Matter"; *Phil. Trans.*, 1870, 333.

18 (p. 11) A. EINSTEIN: "Elementare Theorie der Brownschen Bewegung"; *Z. Elektrochem.*, 1908; **14**, 235: *Ann. Physik*, 1905; (iv.) **17**, 549: 1906; (iv.) **19**, 371.

VON SMOLUCHOWSKI: "Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen"; *Ann. Physik*, 1906; (iv.) **21**, 756.

P. LANGEVIN: "Sur la théorie du mouvement brownien"; *Compt. Rend.*, 1908; **146**, 530.

19 (p. 12) E. CUNNINGHAM: "Terminal Velocity of Spheres falling in a Fluid"; *Proc. Roy. Soc.*, 1910; **A83**, 357.

20 (p. 12) T. SVEDBERG: "Über die Eigenbewegung der Teilchen im Kolloidalen Lösungen"; *Z. Elektrochem.*, 1906; **12**, 853, 909.

21 (p. 12) M. SEDDIG: "Uber die Messung der Temperaturabhängigkeit der Brownschen Molekularbewegung"; *Phys. Z.*, 1908; **9**, 465.

22 (p. 12) J. PERRIN and DABROWSKI: "Mouvement brownien et constantes moléculaires"; *Compt. Rend.*, 1909; **149**, 477.
J. PERRIN: "Les grandeurs moléculaires (nouvelles mésures)"; *Compt. Rend.*, 1911; **152**, 1380.
23 (p 12) M. DE BROGLIE: "Sur des mésures de mouvements browniens dans les gaz, et la charge des particules en suspension"; *Compt. Rend.*, 1909; **148**, 1315.
24 (p. 12) *Idem* "Sur des observations du mouvement brownien dans les gaz à basse pression"; *Compt. Rend.*, 1912; **154**, 112.
R. A. MILLIKAN: "Brownian Movements in Gases at Low Pressures"; *Phys. Rev.*, 1913; (ii.) **1**, 218.
25 (p. 12) H. FLETCHER: "A Verification of the Theory of Brownian Movements and a direct Determination of the Value of *NE* for gaseous Ionization"; *Phys. Rev.*, 1911; **33**, 81.
26 (p. 13) P. SCHERRER: "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen"; *Chem. Zentr.*, 1919; (vi.) **1**, 322. (Abstracted from *Nachr. K. Ges. Wiss. Göttingen*, 1918; 96)
27 (p. 13) J. PERRIN: "Mouvement brownien et réalité moléculaire"; *Ann. Chim. Phys.*, 1909; (viii.) **18**, 5.
28 (p. 14) *Idem*: "L'agitation moléculaire et le mouvement brownien"; *Compt. Rend.*, 1908; **146**, 967.
29 (p. 14) *Idem*: "Grandeur des molécules, et charge de l'electron"; *Compt. Rend.*, 1908; **147**, 594.
30 (p. 15) E. F. BURTON and (Miss) E. BISHOP: "The Law of Distribution of Particles in Colloidal Solution"; *Proc. Roy. Soc.*, 1921; **A100**, 414.
31 (p. 15) A. W. PORTER and J. J. HEDGES: "The Law of Distribution of Particles in Colloidal Suspensions, with Special Reference to Perrin's Investigations"; *Trans. Farad. Soc.*, 1922; **18**, 91: 1923; **19**, 1.

CHAPTER II

THE ELECTRON

8. The Ionic Theory of Solutions

THE study of electrical phenomena is conveniently commenced with the well-established facts connected with the conduction of electricity through aqueous solutions. Pure water is known to be a very bad conductor of the electric current. When certain substances, known as " electrolytes," are dissolved in it, however, the conductivity is greatly increased. If a current is passed through such a solution, certain changes occur, the process being known as " electrolysis." For instance, when an electric current passes between two electrodes placed in an aqueous solution of zinc chloride, the latter is split up into its elements, zinc and chlorine. The zinc travels towards the " cathode," or negative electrode by which (according to convention) the current leaves the solution. The chlorine appears at the " anode," or positive electrode, where the current enters, and travels in the direction opposite to that of the zinc. It may not be difficult to understand that the view gradually gained ground that the current simply maintained a difference of potential between the electrodes, the movement of the zinc and chlorine being responsible for the passage of the current through the solution. Further, since the zinc is attracted to a pole charged negatively, it appears to carry a positive charge, and the chlorine a negative charge. This follows from the well-known fact that unlike charges attract each other. The charged atoms have become known as " ions " (*Gk.* travellers).

The true significance of these simple results was not realized for a considerable period after their discovery. According to the older theory of electrolysis, the applied E.M.F. was thought to be the sole agent in breaking up the molecules of an electrolyte. The experimental facts were, however, strongly against this

view, for, according to it, a minimum E.M.F. would be expected, below which no current should pass, and above which decomposition would set in accompanied by a strong current. Careful experiment, however, showed that electrolytes obeyed Ohm's law, the current being proportional to the E.M.F., no matter how small the latter might be. Clausius deduced from this that no electrical energy is expended in splitting up the dissolved molecules into ions. He therefore assumed that the *electric field simply tended to prevent the recombination of* ions, which already existed in the solution, and to attract them to the electrodes. These ions were supposed to be formed by the impacts between molecules, which, according to the kinetic theory, were continually occurring. This idea seemed to conflict with the experimental fact that the conductivity of solutions increased with dilution.

Arrhenius completely harmonized the theory with experimental results, and also gave a quantitative basis to the subject in his electrolytic dissociation hypothesis. He assumed that a large number of free ions were separated immediately when an electrolyte was dissolved in water. The conductivity depended on the number of ions present, the substance being more ionized in dilute solution. It is easy to understand that the chance of recombination is smaller in dilute solution, if ions are not thought of as formed by impacts between molecules. It is, however, outside the scope of this work to follow the way in which Arrhenius developed his ionic theory to give quantitative account of the properties of solutions.[1]

More than fifty years before this time, Faraday had published his immortal "Experimental Researches in Electricity," in which he had been the first to use the term "ion," and had given the laws which governed the quantitative aspect of the electrolysis of solutions.[2] He found, first, that the weight of substance liberated in electrolysis was strictly proportional to the quantity of electricity Q which passed through the solution, and, further, that for the same Q chemically equivalent weights of different substances were set free. Thus amounts of substances which are chemically equivalent are also electrically equivalent. A current which can liberate 1 gram of hydrogen is capable of setting free 107·1 grams of silver. In the case of zinc chloride, the same current sets free 35·46 grams of chlorine, and 32·68 grams of zinc. If the ionic hypothesis is accepted, then from the known chemical composition of zinc chloride ($ZnCl_2$), there must be twice as many chlorine ions in a

The work of the twentieth century has thus proved Maxwell wrong in his prediction mentioned above, and the atomic nature of electricity now rests upon evidence as strong as that for the atomic nature of matter.

It may be noted that the charges carried by positive and negative monovalent ions are equal to each other, since the molecules of the binary salts from which they are formed and which they reproduce by recombination are themselves neutral.

9. The Charge of an Electron

A little reflection will show that Faraday's results, combined with a knowledge of the value of the Avogadro number N (the number of atoms in a gram-atom or gram-equivalent of a monovalent element) should lead to a determination of the charge borne by a single monovalent ion in electrolysis. The amount of electricity necessary to set free one gram-equivalent of an element is called a "Faraday," and is known with exactness from direct experiment. Further, the atoms of an element liberated in electrolysis must have come from an equal number of ions, so that the charge carried by a single monovalent ion may be obtained by dividing the Faraday by N. As early as 1874, Johnstone Stoney obtained $0{\cdot}3 \times 10^{-10}$ E.S. units for this charge, but the only available value of N at that time was subject to considerable uncertainty. If Perrin's early value of $N = 70 \times 10^{22}$ is used, and the Faraday taken as 9650 E.M. units, or $9650 \times 3 \times 10^{10} = 28{,}950 \times 10^{10}$ E.S. units, a value $4{\cdot}13 \times 10^{-10}$ E.S. units is obtained, which is more than ten times as great, though much nearer that at present accepted. This minute charge is about one hundred thousandth of that which can be detected by a good electroscope.

The first light thrown on this question by direct experiment came from the work of Townsend in 1897, on the charge carried by ions in gases.[5] Two years later, the same worker showed that this charge was equal to that borne by the hydrogen ion in electrolysis. This significant result will occupy attention in the following chapter (section 12). The same conclusion also follows from Millikan's later work given at the end of the present section. It is well to bear this in mind, in considering Townsend's experiment, as it links up the experiments on electrolysis with those about to be described on gases. For the present, it is assumed that electric conduction in gases is explained by the presence of charged ions, by analogy with electrolysis.

Laplace and Lavoisier knew that the hydrogen evolved vhen a metal dissolved in an acid was charged. Enright had hown that the hydrogen given off when iron dissolved in sul›huric acid carried a positive charge.[6] Lodge considered that his charge was carried on the spray, and had been acquired by riction. Townsend showed (loc. cit. above) that this was not he case, by bubbling the evolved gas through flasks containing ›otassium permanganate and sulphuric acid and then through ι tube of glass wool, and showing that the issuing gas still carried ι positive charge, though reduced in amount. The charge was, :herefore, carried by the gas and not by the spray. He also :stablished the important fact that the gases liberated in elec·rolysis were charged. He found that the gases liberated in :he electrolysis of sulphuric acid were charged positively, and rom caustic potash were charged negatively. He showed that :hese charged gases when bubbled through water formed a lense cloud. The density of the cloud increased with the lensity of the charge, and the cloud could be removed by bub›ling through sulphuric acid. He concluded that the gas ions ιad the property of condensing water vapour upon them, :hereby forming tiny charged droplets. He assumed, in what ollows, that the number of droplets equalled the number of ons originally present.

In order to determine the charge carried by the ions of a ;as set free in electrolysis, Townsend measured the following :wo quantities as accurately as possible :—

(*a*) *The total charge carried by unit volume of gas.*—To obtain :his, Townsend measured the charge borne by a known volume ›f gas directly, using a quadrant electrometer. The apparatus was insulated, and the charges induced in a metal covering were recorded.

(*b*) *The number of ions present in unit volume of gas.*—For :his purpose, Townsend formed a cloud by bubbling through water, and passed it into a flask and noted the distance the top ›f the cloud fell under gravity in a measured time. He then ıpplied Stokes' law for the rate of fall, and so calculated the ıverage weight of the droplets. This law, for the fall of spherical ›articles of radius r under gravity when the density of the nedium can be neglected compared with that of the droplets, s

$$v = \frac{2r^2g\sigma}{9\eta} \quad . \qquad (1)$$

where r is given by

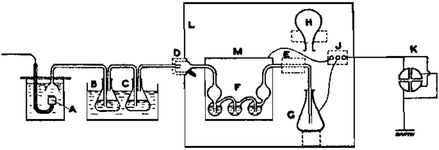
$$m = \frac{4}{3}\pi r^3\sigma \quad . \quad . \quad . \quad . \quad (2)$$

where v is the rate of fall, η the viscosity coefficient of the medium, σ the density, and m the average weight of droplet (cf. equations (4) and (5), p. 11). Knowing the total weight of the cloud, and using the mass m of a droplet obtained from (2), Townsend obtained the number of droplets, which, according

Figure II

APPARATUS FOR DETERMINATION OF ELECTRONIC CHARGE (TOWNSEND)

(*Proc. Camb. Phil. Soc.*, 1897; 9, 346)



A. Platinum electrode where gas is evolved.
B, C. Flasks containing potassium iodide and water respectively, immersed in trough of water at fixed temperature.
D, E. Paraffin block tunnels for insulation.
F. Three bulbs containing sulphuric acid.
G, H, Insulated inductors covered with tin foil.
L. Large metallic screen.
J. Paraffin block, containing three mercury cups, arranged to communicate charges collected on the hollow metal vessel M or on the inductors G, H to the quadrant electrometer K.

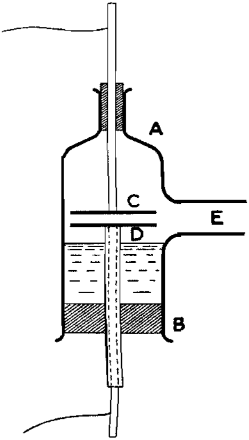
to the assumption mentioned, equalled the number of ions. The weight of the cloud was determined by passing it through a bubbler containing sulphuric acid, and finding the gain in weight. Then, allowing for the calculated weight of moisture necessary to saturate the known volume of gas at the temperature of the experiment, he deduced the required weight. From the results of (a) and (b), he then calculated the charge of a single droplet. See Fig. 2 for arrangement of apparatus. The details were mostly worked out in a later paper, where Townsend gave

droplets possessed the smallest charges. By making observa tions upon this set, then, the results corresponded to the leas

Figure III

APPARATUS FOR DETERMINATION OF ELECTRONIC CHARGE (H. A. WILSON)

(*Phil. Mag.*, 1903; (vi) 5, 431)



A B. Glass tube, 4 cms. diameter, 10 cms. long, containing water in lower part.
C, D. Brass discs, 3½ cms. diameter, serving as electrodes, the space between C and D being illuminated by narrow beam of light.
E. Side tube to expansion apparatus (for producing cloud), and to manometer.

heavily charged droplets, and the assumption that the number of droplets was equal to the number of ions was avoided. Now

the velocity of fall of the cloud be v_1 when gravity alone ts upon the droplets, and v_2 when assisted by the field. In e first case, the force of gravity is mg, where m is the average ight of a droplet, and in the second the force acting is $g + Xe$), where X is the strength of the field, and e the arge on the droplet. Assuming that the velocity is in each se proportional by the same amount to the force acting, ilson wrote:—

$$\frac{mg}{mg + Xe} = \frac{v_1}{v_2} \quad . \quad . \quad . \quad . \quad (3)$$

e obtained m by means of Stokes' Law in a manner similar to at used by Townsend. The mean of eleven results for e was 1×10^{-10} E.S. *units, but the divergence was considerable on* ch side of this mean value.

A short study of the equation given above will show that e pends *on the difference* $(v_2 - v_1)$. *Since this difference was* ver very great in any experiment, the accuracy obtainable, art from other inherent errors of method (such as evaporation the droplets, and consequent variation in mass) was not ecially great. But the introduction of an electrostatic field influence the velocities of charged droplets was important, d led to some remarkable results in the hands of Millikan a tle later. Wilson also measured the rates of fall of the other ts of droplets already mentioned. Assuming that the drops of different sets had the same size, he indicated, beside his incipal set having one ion per droplet, two other sets having and 3 ions per droplet respectively. All the work so far corded in the determination of e was performed in the Cavensh Laboratory at Cambridge, and was assisted by the advice d suggestions of Professor Thomson.

In 1908, Millikan and Begeman repeated Wilson's experient, using a 4000-volt battery. Thus the distances and times *fall of the cloud could be lessened, and the error due to* aporation further reduced. The difference $(v_2 - v_1)$ was also creased. The mean of ten observations was given as $e =$ $\cdot 06 \times 10^{-10}$ E.S. *units, and the results did not diverge so* dely as those of Wilson from the mean value. In the following ar, Millikan published his first observations upon individual oplets.[12] A tube such as that used in Wilson's experiments is surrounded by a chamber containing water slightly above e temperature of the room. The air in the space was ionized exposure to the rays of radium, and a cloud formed in it

by the expansion method. The field was then thrown on between electrodes 0·545 cm. apart in such a direction as to retard the fall of the droplets observed. A small section of the space between the plates was illuminated by a narrow beam from an arc light, and this was viewed through a telescope containing three equally-spaced cross-hairs. It was found that, after a few seconds, by adjusting the field, a certain number of droplets could be made to remain suspended, their tendency to fall under gravity being neutralized by the field, and their presence being manifest as bright points of light. The field was then thrown off, and the times of fall of an individual droplet between the two cross-hair spaces measured as accurately as possible, using a stop watch. Stokes' Law was assumed for the rate of fall, and the principle of the caculation was the same as in Wilson's experiment, v_2 being zero and X negative. The "weighted" mean of six series of experiments gave $e = 4{\cdot}65 \times 10^{-10}$ E.S. units. Since the drop was not moving at the moment the field was thrown off, it was assumed that it was not evaporating. Also, if it had commenced to evaporate during its fall, the time required to fall under gravity through the first space in the cross-hairs should be less than that required for the second space. In general, this was not observed to happen, and thus the error due to evaporation was largely overcome. Further, the concordant results of observation of individual droplets would eliminate the possibility that the values previously obtained for e were mean values of numbers varying among themselves. It was in the course of these experiments that Millikan occasionally noticed, when he had omitted to screen the radium from the chamber, that a sudden movement of a droplet upwards or downwards occurred, indicating that it had captured a positive or negative ion. This led to further developments of the work.

In later experiments, Millikan used drops of oil instead of water droplets.[18] A commercial "atomizer" was employed to produce an oil spray charged electrically by friction in a large chamber. Two brass plates, each 22 cm. in diameter, were placed 16 mm. apart at the bottom of this chamber to serve as electrodes for a 10,000-volt battery, the field of which could be reversed or cut out as required by means of a switch. The upper brass plate contained several tiny pin-holes, through which an oil drop occasionally found its way. The whole apparatus was immersed in an oil bath at constant temperature. The space between the plates was illuminated by a powerful

beam of light, and could be observed through a telescope, somewhat as in the arrangement of the ultramicroscope. The air between the plates was kept stagnant by cutting out the heat rays of the arc, by water cooling and passing through a cell of cupric chloride. The telescope contained two fixed cross-hairs whose distance apart corresponded in a series of experiments to a distance of fall of 1·0220 cm. A drop of oil, appearing as a bright star on a black background, could be made to travel upwards against gravity by throwing on a suitable field in the right direction. Just before it reached the upper plate, however, the plates were shortcircuited, and the drop was allowed to fall under gravity until it nearly reached the lower plate. At this point, the field was again applied, causing the drop to retrace its path. The times taken by the drop to pass downwards under gravity and upwards under the influence of the field between the cross-hairs of the telescope were measured by a stop watch, or a chronoscope.

The results of a very large number of observations, in which the conditions were varied as much as possible, showed that, within the experimental error, for a given droplet under the same conditions, the following held good :—

(1) The time of fall under gravity alone was constant.

(2) The times of rise under a field acting against gravity varied *discontinuously*. Thus the times of rise fell into a definite limited number of groups, those within a group being the same within the experimental error.

The numbers obtained in a definite case will illustrate these points. The average of ten observations of the time of fall of an oil drop under gravity was 59·14 seconds. The times of rise were given as follows: 21·23, 65·52, 65·75, 31·85, 31·72, 20·98, 64·45 and 20·90 seconds. Taking the mean values of those times which are approximately the same, the following three are derived: 65·24, 31·79, and 21·04 seconds. Now, since the distance travelled in these times is in all cases the same, the velocity of the drop is measured by the reciprocal of the time taken. Further, when the drop is urged upwards by the field against gravity, a little consideration will show that the velocity of the drop *due to the field* is equal to its velocity under gravity plus its measured velocity under the two acting together. If, then, the reciprocals of each of the three numbers given above are added to the reciprocal of 59·14 the following numbers are obtained: 0·03224, 0·04837, 0·06444, which are almost exactly in the proportion 2 : 3 : 4. The charges carried by the drop,

being strictly proportional to the velocities due to a given field (equation (4a) below), must, therefore, vary in a simple multiple fashion. A large number of experiments were performed on different drops in different media, which confirmed this conclusion. Here, then, is evidence of a very definite character indicating the existence of that unit of electricity named the electron by Johnstone Stoney. The highest common factor of the velocities as measured above gives a value of this elementary charge in terms of a velocity, for a given drop under fixed conditions of voltage, temperature, pressure, etc. This value in the case cited above would evidently be 0·01612.

The value of e in absolute units, however, must be independent of conditions. Its exact evaluation depends upon the following equation (cf. equation (3), p. 29) :—

$$\frac{v_1}{v_2} = \frac{mg}{Xe_n - mg} \quad . \quad . \quad . \quad . \quad (4)$$

where v_1, v_2 are respectively the velocities under gravity alone and under the field acting against gravity, X is the strength of the field, and e_n the charge on the drop. Rearranging this equation,

$$e_n = \frac{mg}{Xv_1}(v_1 + v_2) \quad . \quad . \quad . \quad (4a)$$

where $(v_1 + v_2)$ is the velocity of the drop caused by the field of strength X acting alone, and where the quantity outside the bracket is constant in a given experiment. The highest common factor of $(v_1 + v_2)$, which may be written $(v_1 + v_2)_1$ should correspond to the case when unit charge is carried, where $n = 1$, and $e_n = e_1$. Thus—

$$e_1 = \frac{mg}{Xv_1}(v_1 + v_2)_1 \quad . \quad . \quad . \quad (5)$$

The evaluation of e_1 will, therefore, depend upon the determination of m, the mass of the drop. Stokes' Law, applied to the fall of the drop under gravity, was used for this purpose, by which (cf. equation (5) above),

$$v_1 = \frac{2gr^2}{9\eta}(\sigma - \rho) \quad . \quad . \quad . \quad . \quad (6)$$

where v_1 is the velocity of fall of the drop under gravity, r its radius, η the viscosity coefficient, and σ, ρ are the densities of the drop and of the medium respectively. The law breaks

down, however, when the radius of the drop becomes comparable with L, the mean free path of molecules in the medium. Cunningham multiplied the value of v_1 as given in equation (6) by a correction term :

$$1 + A\frac{L}{r},$$

where A is a constant. Since L varies inversely as the pressure P of the medium, this term can also be written—

$$1 + \frac{B}{Pr},$$

where B is another constant. Further, for a spherical drop, the mass m is connected with the radius r by the relation—

$$m = \frac{4}{3}\pi r^3(\sigma - \rho) \quad . \quad . \quad . \quad (7)$$

From (5), (6) and (7), m and r can be eliminated, and thus e_1 can be accurately calculated in terms of known quantities, particularly as very reliable determinations of η have been made. This value of e_1 does not allow for the Cunningham correction. If e is the value when this is introduced, a little manipulation shows, as the reader may easily verify, that the following relation holds :—

$$e_1^{\frac{2}{3}} = e^{\frac{2}{3}}\left(1 - \frac{B}{Pr}\right) \quad . \quad . \quad . \quad (8)$$

In this equation, e_1 and P are known, and, therefore, r and B are required to determine e. One method of procedure is as follows. An approximate value of r is obtained by applying equation (6) to faster moving, and therefore larger drops, where the Cunningham correction is not very large. If, then, values of $e_1^{\frac{2}{3}}$ are plotted against $1/Pr$, a linear relationship should be observed, according to equation (8). B can then be obtained approximately from the slope of this line and the intercept on the $e_1^{\frac{2}{3}}$ axis. Equation (6) *with* the Cunningham correction is now used to obtain a more exact value of r. It should be remembered that the correction term $1/Pr$ is a small one, so that, as a matter of fact, not more than two approximations are necessary to obtain r with accuracy sufficient for an exact evaluation of e. When e_1 and $1/Pr$ are known, these can be plotted against each other. A study of equation (8) shows that when $1/Pr = 0$, $e_1 = e$, so that a value of e can be obtained

from this line. In order to reduce the error in e due to a constant error in the constant B as far as possible, Millikan studied a number of drops of such a size that the correction factor was quite small. The mean value of $e^{\frac{2}{3}}$, taking $\eta = 0{\cdot}0001824$, for 23 drops was $61{\cdot}085 \times 10^{-8}$, which gave $e = 4{\cdot}774 \times 10^{-10}$. In 1917, further experiments were carried out, using an entirely new apparatus (see Fig. 4).[14] The times were measured by a printing chronograph controlled by an astronomical clock. The results on 25 drops were recorded. Using the value of $\eta = 0{\cdot}00018227$ obtained by Harrington (1916), the final value of e happened to be exactly the same as that recorded in 1913. The result given is:—

$$e = 4{\cdot}774 \times 10^{-10} \pm 0{\cdot}005 \times 10^{-10} \text{ E.S. units,}$$

and

$$N = 6{\cdot}062 \times 10^{23} \pm 0{\cdot}006 \times 10^{23},$$

the latter number being obtained from—

$$Ne = 9649{\cdot}4 \times 2{\cdot}9990 \times 10^{10} \text{ E.S. units.}$$

The corresponding mass of the hydrogen atom is—

$$m_{H} = 1{\cdot}662 \times 10^{-24} \pm 0{\cdot}002 \times 10^{-24} \text{ gram.}$$

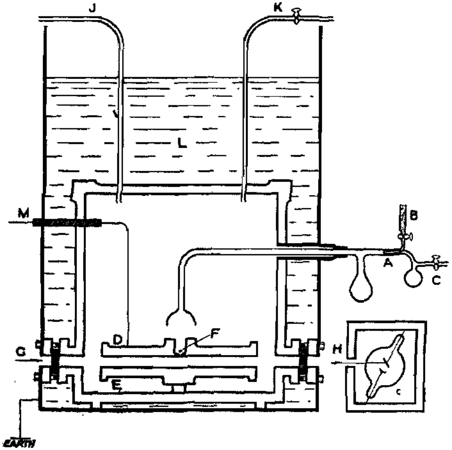
The uncertainty in these values depended mainly upon the measurement of the cross-hair distance (needed for v_1), and on the value of the viscosity coefficient.

The evidence reviewed in this section has been treated in considerable detail, because it is specially important in connection with the subject of atomic structure. The work of Millikan, by itself, definitely proves the existence of electrons. It may now be briefly noted that the work of others is entirely in harmony with this view. Planck, on theoretical grounds, obtained $e = 4{\cdot}69 \times 10^{-10}$ E.S. units. Rutherford and Geiger, from the counting of alpha particles, gave $e = 4{\cdot}65 \times 10^{-10}$ E.S. units (1908) and Regener, by the same method, $e = 4{\cdot}79 \times 10^{-10}$ E.S. units. These experiments will be more suitably considered at a later stage. Other determinations by Perrin, Ehrenhaft, de Broglie and Moreau published in 1908 and 1909, yielded values of e more or less nearly approaching the above values. The Bohr theory of the atom, which has been remarkably successful in accounting for the optical spectra of atoms, also involves the same constant. The belief in the atomic nature of electricity is, therefore, securely founded. A smaller charge than that of the electron has not been proved to exist. Ehrenhaft

FIGURE IV

APPARATUS FOR DETERMINATION OF ELECTRONIC CHARGE (MILLIKAN)

(*Phil. Mag.*, 1917; (vi) 34, 5)



A. Atomizer fed from B with high grade watch oil, blown by clean dry air through C.
D, E. Circular condenser plates, 22 cms. diameter, 15 mms. apart (latter distance exaggerated in figure).
F. Five holes in plate D, 0·25 mm. diameter, for admission of oil droplets into space between the plates.
G. Beam of light from an arc, filtered through water and free from heat rays.
H. Beam of X-rays, for changing charge on droplet.
J, K. Tubes leading to manometer and pump respectively.
L. Oil in bath surrounding apparatus, to maintain constant temperature about 23° C.
M. Wire to 10,000-volt battery, voltmeter, reversing switch, etc.

The droplet was observed through a telescope, whose

has suggested the possibility of a "sub-electron,"[15] but this has been vigorously contested by Millikan.[16] A clear case *has not up to the present been made out for this idea, and more* direct evidence would be needed before it could be accepted.

Independent electrical units exist in two forms, bearing charges of opposite sign. The word "electron" is, however, often, rightly or wrongly, limited to the case when the charge carried is negative. In what follows, reference will be made *either* to positive and negative electrons, *or* to "proton" and electron, in which case "proton" must be taken to be an abbreviated form of "positive electron," and "electron" will then refer to the negatively-charged carrier. This is adopted for convenience, and it may be remembered that, as emphasized by Millikan, the term "electron" logically comprehends the unit of either sign.

10. The Mass of the Electron

In order that the information given in this chapter shall be as complete as possible with regard to the electron, the results obtained as to the masses of positive and negative electrons will be given, though the evidence must be reserved to the following chapter.

Since the electron is the fundamental unit of electricity, which is a form of energy, the reader who meets the idea of mass in connection with it for the first time may encounter some difficulty. Yet, it will be seen, as the subject is developed, that the old hard and fast distinction between matter and energy, on the ground that of the two entities the former alone possesses mass, has been largely broken down by the modern physicist. Indeed, it will appear that it is only by assigning mass to the electron that we can account for the mass of matter. It requires energy to change the speed of an electron, because it has inertia or mass. Moreover, if electric currents consist of streams of moving electrons, the inertia of the electron explains the *experimentally established inertia of the electric current.* Further, according to the hypothesis of relativity, the mass of a body is not an absolutely invariable quantity as at one time supposed, but depends upon the state of motion of the body (section 57, p. 271).

The value of the mass of the negative electron depends upon the measurement of the ratio of its charge to its mass (usually written e/m). The value of this ratio was determined by

Wiechert and Thomson independently in 1897 (section 14). The further experiments of Kaufmann and Bucherer and others have established the fact that this ratio, apart from relativity corrections, is a universal constant, having the value $1{\cdot}77 \times 10^7$ E.M. units per gram. Using Millikan's value of e, and converting E.M. into E.S. units by multiplying by 3×10^{10},

$$m = \frac{4{\cdot}774 \times 10^{-10}}{1{\cdot}77 \times 10^7 \times 3 \times 10^{10}}$$
$$= 9 \times 10^{-28} \text{ gram.}$$

The mass of the negative electron is thus considerably smaller than that of the hydrogen atom. It will be seen that $m : m_H = 1 : 1800$ approximately. The mass of an electron may be considered to be entirely electromagnetic. This has been established by Bücherer, by measuring the rate of variation of mass with speed for negative electrons emitted by radium preparations.[17] Such electrons move with speeds approaching that of light, and the relativity correction becomes appreciable. The observed variation in mass agreed with that calculated on the assumption that the mass was entirely of electrical origin.

With regard to the mass of the positive electron, the results of experiment show that the e/m ratio for a singly charged positive ion in gases is never greater than that for the hydrogen ion in electrolysis. Further, the modern physicist regards a neutral atom of hydrogen as consisting of one positive and one negative electron only. Then, since the mass of the negative electron is small compared with that of the hydrogen atom, the mass of the positive electron or proton is approximately equal to that of this atom. It is a striking fact that the two units should differ so considerably in this respect. The mass of the proton is probably also electromagnetic in origin. The evidence omitted here as to the e/m ratios and the constitution of the hydrogen atom will be found on pages 52 and 93.

11. The Speeds and Sizes of Electrons

The speeds of negative electrons in the discharge tube and when emitted by radioactive substances are so great that they approach the velocity of light. Thomson's work on cathode rays must be consulted in this connection (see Chapter III).

In 1881, Thomson showed that the electromagnetic mass of a small charged particle is given by the relation—

$$m = \frac{2e^2}{3r} \quad . \quad . \quad . \quad . \quad (9)$$

where r is the radius of the particle.[18] Knowing m and e, it is possible to calculate the radii of positive and negative electrons, if it is true that the mass in each case is entirely due to the charge carried. In this way, r for the negative electron is found to be $1 \cdot 9 \times 10^{-13}$ cm. Recalling that estimates of the radius of the hydrogen atom lead to a value about 10^{-8} cm., it is clear that the negative electron is not only much lighter but also *much smaller than this atom.* With regard to the positive electron, it will be observed that if its mass is greater than that of its negative partner, then according to equation (9) above, its radius must be less in the same proportion. On this basis, then, it must be supposed that the greater mass of the proton is connected with the fact that the same charge is distributed upon a smaller sphere. If the mass of the proton is about 1800 times as great as that of the electron, then its radius must be only 1/1800 as much.

A critical résumé of the methods of measuring the dimensions of molecules, atoms and ions has been given by Herzfeld.[19] With regard to the exceedingly small numbers involved, W. H. Bragg has made the suggestion that the Ångstrom unit of *length* (10^{-8} *cm.*) *should be made the basis of a unit of area* 10^{-16} cm.^{2}, of volume 10^{-24} cm.^{3}, and of mass 10^{-24} gram.[20] This would seem worthy of general adoption. The mass of a hydrogen atom expressed in such units would be 1·66.

Values have now been given for the magnitudes relating to atoms and electrons which are necessary for the present purpose. It may, therefore, be convenient for reference if these are collected together as in Table II.

TABLE II

Magnitudes Relating to Atoms and Electrons

Avogadro number N	$6 \cdot 06 \times 10^{23}$
Mass of hydrogen atom and positive electron	1·66 A.U. of mass
Velocity of hydrogen molecule at 0° C.	1·8 kilometres per sec.
Diameter of helium atom . . .	2 A.U.
Charge of the electron . . .	$4 \cdot 77 \times 10^{-10}$ E.S. units. $1 \cdot 59 \times 10^{-20}$ E.M. units.
Mass of the negative electron . .	$8 \cdot 96 \times 10^{-28}$ gram.
Radius of negative electron	$1 \cdot 9 \times 10^{-13}$ cm.
e/m for negative electron . . .	$1 \cdot 774 \times 10^{7}$ E.M. units per gram.

These are magnitudes of which the mind can form no conception whatever. They can be more easily thought of relatively; for example, by remembering that the mass and radius of the hydrogen atom are respectively about 1800 and 100,000 times as great as the corresponding magnitudes in the case of the negative electron.

REFERENCES: (II)

See Nos. 3 and 20 in Bibliographical List at end of book

1 (p. 22) S. ARRHENIUS: "Über die Dissociation der in Wasser gelösten Stoffe"; *Z. Phys. Chem.*, 1887; **1**, 630.

2 (p. 22) M. FARADAY: "Experimental Researches in Electricity" (Series 3, 4, 5, 7, 8); *Phil. Trans.*, 1833; Part I, 23; Part II, 507, 675: 1834; Part I, 77; Part II, 425.

(p. 23) H. L. F. VON HELMHOLTZ: "On the Modern Development of Faraday's Conception of Electricity"; *J. Chem. Soc., Trans.*, 1881; **39**, 277. See also W. RAMSAY: "The Electron as an Element"; *J. Chem. Soc., Trans.*, 1908; **93**, 774.

3 (p. 23) G. JOHNSTONE STONEY: "On the Physical Units of Nature"; *Phil. Mag.*, 1881; (v.) **11**, 384.

4 (p. 23) *Idem*: "On the Cause of Double Lines and of Equidistant Satellites in the Spectra of Gases"; *Trans. Roy. Dub. Soc.*, 1891; (xi.) **4**, 563.

5 (p. 24) J. S. TOWNSEND: "On Electricity in Gases and the Formation of Clouds in Charged Gases"; *Proc. Camb. Phil. Soc.*, 1897; **9**, 244.

6 (p. 25) J. ENRIGHT: "On Electrifications due to the Contact of Gases with Liquids"; *Phil. Mag.*, 1890; (v.) **29**, 56.

7 (p. 27) J. S. TOWNSEND: "Electrical Properties of Newly Prepared Gases"; *Proc. Camb. Phil. Soc.*, 1897; **9**, 345.

8 (p. 27) J. J. THOMSON: "On the Charge of Electricity carried by the Ions produced by Röntgen Rays"; *Phil. Mag.*, 1898; (v.) **46**, 528.

Idem: "On the Masses of the Ions in Gases at Low Pressures"; *Phil. Mag.*, 1899; (v.) **48**, 547.

9 (p. 27) C. T. R. WILSON: "Condensation of Water Vapour in the Presence of Dust-free Air and other Gases"; *Phil. Trans.*, 1897; **A189**, 265.

Idem: "On the Condensation Nuclei produced in Gases by the Action of Röntgen Rays, Uranium Rays, Ultra-violet Light and other Agents"; *Phil. Trans.*, 1899; **A192**, 403.

10 (p. 27) J. J. THOMSON: "On the Charge of Electricity carried by a Gaseous Ion"; *Phil. Mag.*, 1903; (vi.) **5**, 346.

11 (p. 27) H. A. WILSON: "A Determination of the Charge on the Ions produced in Air by Röntgen Rays"; *Phil. Mag.*, 1903; (vi.) **5**, 429.

12 (p. 29) R. A. MILLIKAN: "A New Modification of the Cloud Method of determining the Elementary Electrical Charge and the most Probable Value of that Charge"; *Phil. Mag.*, 1910; (vi.) **19**, 209.

13 (p. 30) *Idem*: "The Isolation of an Ion, a Precision Measurement of its Charge, and the Correction of Stokes' Law"; *Phys. Rev.*, 1911; **32,** 349.
14 (p. 34) *Idem*: "A new Determination of *e*, *N* and Related Constants"; *Phil. Mag.*, 1917; (vi.) **34,** 1.
15 (p. 36) F. Ehrenhaft: "Die Quanten der Elektrizität"; *Ann. Physik*, 1914; (iv.) **44,** 657.
16 (p. 36) R. A. Millikan: "Die Existenz eines Subelektrons?"; *Ann. Physik*, 1916; (iv.) **50,** 729.
17 (p. 37) A. H. Bucherer: "Die experimentelle Bestätigung des Relativitätsprinzips"; *Ann. Physik*, 1909; (iv.) **28,** 513.
18 (p. 38) J. J. Thomson: "On the Electric and Magnetic Effects produced by the Motion of Electrified Bodies"; *Phil. Mag.*, 1881; (v.) **11,** 229.
19 (p. 38) K. F. Herzfeld: "Bericht uber die Grösse der Molekule, Atome und Ionen, und die Methoden zu ihrer Bestimmung"; *Jahr. Rad. Elekt.*, 1922; **19,** 259.
20 (p. 38) W. H. Bragg: "The Structure of Organic Crystals"; *Proc. Phys. Soc.*, 1921; **34,** 33.

CHAPTER III

ELECTRICITY IN GASES

12. The Mechanism of Gaseous Conduction

IT has been necessary in the previous chapter to speak of gaseous ions as carriers of electricity. Some evidence for the existence of ions in solution has been given, and it was sufficient, for the purpose of explaining the work of Townsend and others, to assume that a gas contained ions which behaved in an analogous fashion. The leading features of gaseous conduction must now be considered, and it will be seen that, while they are in some respects distinct from those of electrolysis, resemblances also exist.

Gases under normal conditions are well known to be excellent insulators of electricity. Under reduced pressure, however, they permit the passage of an electric discharge. One of the far-reaching results of this fact was the discovery, in 1895, of Röntgen rays, or X-rays. It was soon observed that a charged and insulated electroscope lost its charge when exposed to these rays, which had caused the air near the electroscope to become conducting. Not long after this, other rays, including those from radium, were found to possess a similar property. It has been already noticed that the gases given off in electrolysis of certain solutions are slightly conducting. Moreover, C. T. R. Wilson, following up the work of Linss and of Elster and Geitel, proved that the leaves of a charged insulated electroscope slowly collapsed in the presence of dust-free air in the absence of any agency known to bring about conduction.[1] This showed that air is not a perfect non-conductor at normal pressure, so that gradual leakage occurs from a charged body, even when the insulation of its supports is complete.

The action of X-rays in bringing about the conductivity of air was studied by Thomson and Rutherford in 1896.[2] It was

found that the conductivity induced was temporary, and disappeared when the rays were shielded. It could also be destroyed by passing the gas through a plug of glass wool, or through the space between two plates charged to a sufficiently high difference of potential. In the latter case, as the potential difference was increased, the gas between the plates being kept under the influence of the rays, the current passing gradually rose to a maximum or "saturation" value. It appeared from these early experiments that the conductivity induced in gases by X-rays was due to charged particles of both signs which could be removed by filtration, or attracted to their appropriate electrodes. The saturation current was observed when the gas "ions" produced were swept to the electrodes as fast as they were formed. This current depended directly upon the number of conducting particles produced by the rays. Further, the disappearance of conductivity when the rays were removed was attributed to recombination of positive and negative ions, or to their diffusion and discharge on the walls of a containing vessel.

An important step was made in 1900 when Townsend published a paper which completed the experimental evidence that the charge on a gaseous ion was equal to that carried by the hydrogen ion in electrolysis. The proof was developed in the following way. First, Thomson deduced a relation from the kinetic theory of gases for the velocity of a small charged body moving through a gas under the influence of an electric field, which may be written as follows :—[8]

$$u_x = \frac{XeD}{mK} \quad . \quad . \quad . \quad . \quad (1)$$

where u_x is the velocity of the ion under a field of intensity X, e is its charge, m its mass, K the ratio of pressure to density for the ion, and D is the "coefficient of diffusion" of the ions in the uncharged gas. Further, u_x/X is the velocity under a potential gradient of one volt per cm., a quantity known as the "ionic mobility" u. Then, if n is the number of molecules per c.cm. of gas, putting $K = P/nm$, assuming the pressure of the ion to be the same as the pressure P of the gas,

$$ne = \frac{uP}{D} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The value of ne depends upon u, D and P, and measurements of u and D are needed, since P is readily determined. A method

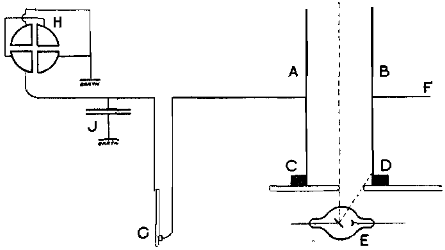
of determination of u was devised by Rutherford in 1897, and of D by Townsend in 1900.

(*a*) *The determination of ionic mobility*.—In Rutherford's method for ions in air, two large parallel plane plates were placed, 16 cms. apart, on insulating supports[4] (see Fig. 5). An X-ray bulb was placed in such a position that only one-half of the air, i.e. 8 cms. thickness, was exposed to its influence.

FIGURE V

APPARATUS FOR IONIC MOBILITY DETERMINATION (RUTHERFORD)

(*Phil. Mag.*, 1897; (v) 44, 436)



A, B. Large plane plates, 16 cms. apart, resting on insulating blocks C, D.
E. X-ray bulb, arranged so that radiation falls on half of space between A and B.
F. Wire to 220-volt battery.
G. Contact lever, knocked away by the swing of a pendulum, thereby breaking the circuit containing electrometer H.
J. Condenser to increase capacity of circuit G H.

The plate adjoining this half was connected to one terminal of a 220-volt battery, the other pole being earthed. The other plate was connected through a contact lever to one pair of quadrants of an electrometer, the other pair being earthed. A pendulum interrupter was arranged to set the bulb in action, and after a short interval of time to break the electrometer circuit by striking the contact lever. The time interval could

be derived from the swing of the pendulum and the distance between the switches. It was found that there was only a small deflection of the electrometer until the time interval had been increased to a definite amount, after which the deflection increased rapidly. This critical time interval was assumed to correspond with the time taken for the ions between the plates to travel the 8 cm. distance screened from the rays. Rutherford found this time to be 0·36 second. The velocity of the ions approaching the screened plate was, therefore, 8/0·36 cm. per second under a potential gradient of 220/16 volts per cm. The velocity under unit potential gradient is thus about 1·6 cms. per second, and this is the ionic mobility as defined above. He found the mobilities of positive and negative ions in air to be the same by this method.

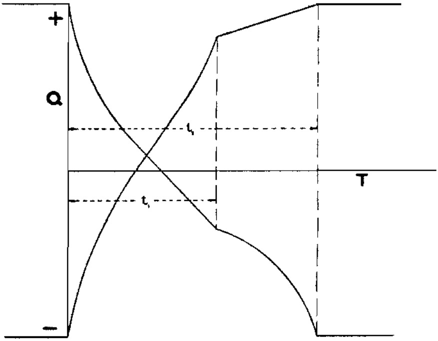
Other ways of measuring ionic mobility were described by Zeleny in 1901,[5] and by Langevin in 1903.[6] Langevin's method, while not so direct as that of Rutherford, appears to be capable of greater accuracy. The air between two parallel plates is completely ionized by an instantaneous flash of X-rays. The plates are connected, as in Rutherford's experiment, to a battery and an electrometer respectively. The pendulum is replaced by a falling weight which actuates two keys in a vertical line, the upper one causing the X-ray flash, and the lower changing the sign of the charged plate. The time interval between the two events is recorded by knowing the distance between the two keys, and using the value of the acceleration due to gravity. The time intervals are varied, and the corresponding charges are read off on the electrometer. In this way, a curve is obtained of the form shown in Fig. 6 (Langevin). It will be seen that there are two breaks in the curve. These breaks are connected with the inequality of the velocities of positive and negative ions, which Rutherford had supposed to be equal. The first break corresponds to the point at which all the faster moving ions have been removed, and the second to the point at which the remaining slower ions have also been discharged. After this, increasing the time will not increase the charge recorded by the electrometer. The former time interval is, therefore, that taken by the faster ions to travel the distance between the plates, and the second (reckoned from the commencement of the experiment) is that taken by the slower ions. The mobilities of the two kinds of ions can then be calculated from the times taken from the curve, the distance between the plates and the constant potential difference as in

Rutherford's experiment. The form of the curve showed that the charge recorded by the electrometer changes its sign before the first break is reached. Further, at low pressures, it was found that in the gases studied the negative ion possessed the greater speed.

FIGURE VI

TIME-CHARGE CURVE (LANGEVIN)

(*Ann. Chim. Phys.*, 1903; (vii) 28, 503)



Charge Q plotted vertically, and time T horizontally. The two halves of the curve correspond with charges of opposite sign on the charged plate. The time t_1 corresponds with the removal of the swifter ion, and t_2 with that of the slower ion. From these times, the distance between the plates and the field strength, the ionic mobilities may be calculated.

(*b*) *The measurement of the diffusion coefficient of ions.*—It has already been pointed out that the disappearance of ions when an ionizing influence is removed may be attributed to two causes. First, recombination of the ions of opposite sign to form neutral molecules may occur. This will normally be the preponderating influence. Secondly, there is diffusion to the walls of the containing vessel. Townsend devised an apparatus which rendered

the recombination effect the smaller of the two.[7] He obtained a uniform stream of gas which was subjected to the influence of X-rays. After ionization, the stream was passed through some fine metal tubes, the bore of which was adjusted so that the number of ions coming into contact with the sides was large compared with the number removed by recombination. Townsend determined the reduction in conductivity produced, and after making allowance for those ions lost by recombination was able to calculate the value of D. It will be clear without detailed analysis that if the diffusion of the ions, which is measured by D, is large, then a large proportion of them will come into contact with the walls of the tube, and a greater reduction in conductivity will occur than in a case when the diffusion is smaller. Townsend's results for dry air were :—

$$D(+) = 0{\cdot}028, \quad D(-) = 0{\cdot}043. \quad \text{Mean} = 0{\cdot}037.$$

(*c*) *The calculation of* ne *for ions in air.*—Townsend used the result of Rutherford on ionic mobility in air quoted above, i.e., $u = 1{\cdot}6$ cms. per second under a potential gradient of one volt per cm. (which is 1/300 in E.S. units), and the above mean value of $D = 0{\cdot}037$, substituting these in equation (2), page 42. The pressure P was the normal atmospheric $= 76$ cms. of mercury, or $76 \times 13{\cdot}6 \times 981 = 10^6$ C.G.S. units approximately, so that—

$$ne = \frac{3 \times 10^8 u}{D} = \frac{3 \times 10^8 \times 1{\cdot}6}{0{\cdot}037}$$
$$= 1{\cdot}3 \times 10^{10} \text{ E.S. units} \qquad \text{(i)}$$

The value of nE for the hydrogen ion in electrolysis was found as follows. Experiment had shown that 1 E.M. unit of electricity liberated 1·23 c.cms. of hydrogen at 15° C. and normal pressure, so that, since each molecule was derived from two discharged ions,

$$2 \times 1{\cdot}23\, nE = 1 \text{ E.M. unit,}$$
or,
$$2{\cdot}46\, nE = 3 \times 10^{10} \text{ E.S. units,}$$
whence
$$nE = 1{\cdot}22 \times 10^{10} \text{ E.S. units} \qquad \text{(ii)}$$

The agreement between these values was regarded as sufficiently good to justify the conclusion that, since n was the same in the two cases, the charge on the ions produced by Röntgen rays in air was equal to the charge on the hydrogen ion in a liquid electrolyte, i.e., $e = E$. Townsend also calculated the value of the product ne for oxygen, carbon dioxide and hydrogen, using values of u for these gases given by Rutherford, obtained

by a different method from that given under (*a*) above. The results justified a more generalized form of the conclusion already given. Further, it has been observed that the charge carried by a monovalent ion in solution is that of the electron. This may be verified by putting $n = N/22{,}400 = 2{\cdot}7 \times 10^{19}$ in (ii) above. Hence an electron is also carried by a singly charged ion in gases.

These results may now be grouped together as follows, and applied to build up a hypothesis of gaseous ionization.

(*a*) The value of ne for negative gaseous ions is the same as for singly charged ions in electrolysis. This implies that the same fundamental unit of charge is concerned in the two cases. Further, the value of e, calculated by using an independent value of n, shows that this unit is the electron.

(*b*) The value of ne for positive ions was found to be slightly greater than that for negative ions. It was, however, supposed that the two charges were really the same, the divergence being due to experimental error. Townsend later modified this conclusion in considering results based upon a new method of determining D.[8] Nevertheless, it seems to be almost universally accepted that, in general, when ionization is induced in a gas, singly charged positive and negative ions are formed.

(*c*) The diffusion coefficients of positive and negative ions at ordinary pressure are of the same order of magnitude in all cases. It must, therefore, be supposed that each kind of ion possesses approximately the same mass.

(*d*) The absolute values of the diffusion coefficients of ions are, in general, smaller than those of uncharged molecules. This has been supposed to indicate that a gaseous ion consists of a cluster of molecules held together with a single charge. If this is so, then, since the diffusion coefficient of positive ions in air is less than than of negative ions, the positive cluster appears to be the larger of the two. The cluster theory has, however, been much criticized, notably by Wellisch.[9] An alternative theory is that the mean free path is modified by the charge carried.

(*e*) The effect of lowering the pressure upon mobility is found to be somewhat different for positive and negative ions in gases, using experimental methods such as those of Langevin and enclosing the gas in an air-tight chamber. For positive ions, the product ionic mobility times pressure (uP) is constant down to very low values of P. With negative ions, however, this product begins to increase below about $P = 10$ cms. mercury. The mobility of an ion may be shown to vary directly as the mean

free path of the medium, which itself varies inversely as tl pressure, according to the kinetic theory of gases, so that would be expected to be inversely proportional to P, i.e., u would be constant. The behaviour of negative ions appear therefore, to demand special explanation. There is evidentl some characteristic difference in the effect of reduction pressure upon the two kinds of ions.

A theory of gaseous ionization may now be suggested o the basis of the points (*a*) to (*e*) above. From (*a*) and (*b* ionization is, in general, brought about by the detachment of single electron from a neutral molecule of matter, leaving th residue oppositely charged. Further, it would appear from (*c* that this electron cannot remain free for a long period, and ha a tendency to attach itself to a neutral molecule, the repetitior of this process producing large numbers of ions of both signs which possess approximately the same mass. If clusters ar formed, as mentioned under (*d*), both kinds of ions have a furthe tendency to attract uncharged molecules. The distinct behaviour of negative ions noted in (*e*) under reduced pressure, indicates that the electron whose movement takes place during ionization is the negative variety. As the pressure is reduced, an increasing proportion of negative electrons remain free without attaching themselves to neutral molecules. This light and tiny negative carrier, once free from its relatively heavy burden of a molecule of gas, has high mobility, and thus the product uP increases for negative ions as the pressure is reduced. These conclusions are in harmony with results obtained in the discharge tube. It will appear that under very low pressures negative electrons are found free, travelling with immense velocity, as "cathode rays." Positively charged molecules and atoms are also found in such circumstances.

The passage of electricity through a gas is to be explained, as in the case of electrolysis, by the movements of ions to their respective electrodes, where they are discharged. The process continues by other molecules becoming ionized (if an ionizing influence is present). Under normal conditions, the conductivity of a gas is not zero, hence a few ions must be present, possibly formed under the influence of radioactive matter in the earth's crust. Recombination to form neutral molecules must also be occurring, so that the number of ions present depends on the position of equilibrium between two opposing processes. The influence of X-rays or other cause of ionizatioı is to displace this equilibrium in the direction favouring the

formation of ions. When the ionizing influence is removed, recombination becomes in excess of ionization until the normal state of equilibrium is attained.[10]

A conclusion of considerable importance for the present subject must now be stated. If the above theory of ionization is accepted, then there appears to be direct evidence of *the existence of negative electrons in matter.* Since a molecule breaks up, yielding an electron, the molecule must have held that electron in some way as part of its structure. An important distinction between ion formation in solutions and gases may here be observed. In solutions, ions are formed from compounds only, whereas in gases ionization occurs in pure gases like oxygen and hydrogen, or even in monatomic gases such as argon and helium. The distinction between matter and electricity appears to a certain extent to be broken down, if the units of electricity enter into the composition of matter. Yet no other satisfactory explanation of the facts is available, and other evidence will be brought to light as we develop the subject that these small charged particles are part of a fabric which was at one time considered to possess an entirely different fundamental nature from that of electricity.

13. The Discharge at Low Pressures

The present section reviews, in a general manner, the experimental observations of electric discharges through gases at low pressures. The various radiations are named, their more detailed explanation being reserved to the remainder of the chapter.

The phenomena of the discharge tube are well known.[11] At first, under normal pressure, the gas appears not to conduct a current at all. As evacuation proceeds, a glow is formed in the tube, which gradually breaks up into striæ. Then a glow appears on the cathode, with a dark space (observed by Faraday) before it. This dark space enlarges towards the anode, and later the glow on the cathode becomes detached, leaving a second dark space behind it, known as "Crookes' dark space." There is, especially at lower pressures, vivid fluorescence on the walls of the tube, but, as evacuation is continued, the dark space gradually fills the whole of the tube. These results naturally aroused much interest, and other facts were gradually discovered. If two platinum wires are sealed in near the cathode, it is found by connecting them to opposite quadrants

of an electrometer, and by taking readings when the wires are at different distances from the cathode, that at low pressures there is a sudden fall of potential near this electrode. The chief interest, therefore, centres round the cathode. Indeed, the position of the anode appears to matter but little, and the rays which leave the cathode may not reach it directly if it does not happen to lie in their direction. If, however, the anode is placed opposite to the cathode, and an obstacle placed in front of it, the obstacle glows brilliantly, and a shadow is thrown on the anode, apparently due to the stoppage of rays travelling towards it.[12] These rays have been called "cathode rays." To anticipate a little, the evidence supports the view that they consist of swiftly-moving, negative electrons, and Crookes' dark space has been attributed to their mean free path before collision with other particles. The luminosity and striæ are considered to be evidences of local ionization, where collisions are of frequent occurrence. If an obstacle is placed in front of the cathode, shadows are formed in both directions, showing that rays are also approaching it. If a hole is made in the cathode, then these rays can pass through it, constituting "positive rays." Moreover, there is a third kind of radiation in the tube. When the Crookes' space fills the whole tube, the walls of the tube exhibit fluorescence, and an obstacle in it glows brightly. This effect is due to a distinct type of radiation, known as "Röntgen rays," or, more usually, as "X-rays." These appeared to be the result of the impact of the cathode rays on an object placed in their path.

14. Cathode Rays

The properties of cathode rays are briefly as follows. First, they leave the cathode normally to its plane, and travel in straight lines, as witnessed by their behaviour towards obstacles, and the nature of the shadows produced. Second, they can turn light wheels or vanes placed in their path. This fact does not prove that they consist of a stream of particles, however, as Lebedew has shown that an electromagnetic radiation can produce a similar effect. Further, they possess remarkable penetrating power towards matter, and can travel through about an inch of air. They can also pass through thin sheets of aluminium or gold leaf. Lenard studied the penetration of the rays in air by causing them to pass outside the tube in which they were generated through a small aluminium window.[13] The rays are deflected by a magnetic field.[14] Crookes passed a

pencil of the rays on to a mica film covered with phosphorescent powder, and brought up an ordinary magnet. The track of the rays (visible on the mica) was seen to be curved. In 1895, Perrin showed that when cathode rays fell upon a small insulated vessel (known as a " Faraday cylinder ") it received a negative charge.[15] Lastly, in 1897, Thomson showed that in high vacuum they were deflected by an electrostatic field, the direction of deflection being consistent with the view that the cathode stream consisted of particles bearing a negative charge. The German school of physicists tended towards the conclusion that the phenomenon had an æthereal nature.[16] It has been stated that the rays were found to travel through ordinary air a distance comparable with an inch, whereas in a distance of a thousandth of an inch atoms of matter would suffer many collisions and so be stopped. Crookes had, however, as far back as 1880, suggested that these rays consisted of matter in a " fourth state," i.e. neither solid, liquid, nor gaseous.

Now, if the charged particle theory was correct, the particles should possess a finite mass in order to account for their deflection in a magnetic field. Wiechert, in 1897, successfully measured the ratio of charge to mass for the supposed particles. In the same year, Thomson also tested the theory experimentally.[17] The principle adopted was that of applying electric and magnetic fields in such a way as to balance their influences, so that no deviation of the rays occurred. For this purpose, it was necessary to apply the two fields at right angles to each other. The rays, after leaving the cathode, were passed through slits in two brass discs to limit them to a narrow pencil. The electric field was applied by two parallel plate electrodes, one of which was charged to a suitable potential, and the other earthed. The magnetic field was applied by means of a small electromagnet, whose poles were placed at right angles to the plate electrodes. The effect on the pencil of rays was observed by placing a screen of barium platinocyanide at the far end of the tube, a spot of light on this screen indicating their point of impact. The anode was placed in a side tube. Thomson then adjusted the fields until the spot of light on the screen returned to its undeflected position. The arrangement is shown in Fig. 7.

When the state of balance is obtained, analysis shows that, if X, H are the strengths of the electric and magnetic fields respectively, and v is the velocity of the particles,

$$v \doteq \frac{X}{H} \quad . \quad . \quad . \quad (3)$$

and, *further*, that if the magnetic field is used by itself so that the rays are bent into a circular path of radius r, then

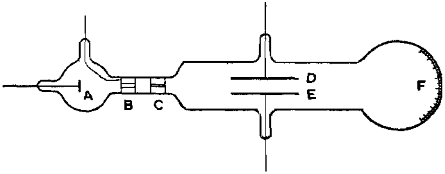
$$\frac{e}{m} = \frac{v}{Hr} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus, v may be obtained from equation (3) and substituted in (4) to obtain the value of the e/m ratio. Thomson showed that this ratio had a definite value *independent of the nature and*

FIGURE VII

EXPERIMENT ON CATHODE RAYS (THOMSON)

(*Phil. Mag.*, 1897; (v) 44, 296)



A. Cathode from which rays pass through the slit in the anode B (earthed) and then through the narrower slit in the metal plug C (also earthed).

D, E. Parallel aluminium plates, 5 × 2 cms., 1·5 cms. apart, serving as electrodes for electric field.

F. Scale pasted on the outside of tube, to measure deflection of phosphorescent patch produced by the rays.

The magnetic field was applied by means of a small electromagnet, placed with its poles at right angles to the plates.

pressure of the gas in the tube. This definitely established the particle theory. The subsequent work of Kaufmann and others has shown that the value of the ratio given by Thomson was somewhat low, and the mean of the best recent observations is $e/m = 1{\cdot}77 \times 10^7$ E.M. units per gram, and $v = 3 \times 10^9$ cms. per second, or about one-tenth of the velocity of light.

The nature of the cathode ray particles, which move with such immense velocity, still remains to be discussed. Evidence

has been already advanced that certain definite particles, namely, negative electrons, are present when a current is passed through a rarified gas. It is, therefore, reasonable to assume that at very low pressures negative electrons are shot away from the cathode with high velocity. The origin of the rays has been recently discussed by Ratner.[18]

Thomson realized that this intimate association of "corpuscles" with matter in the discharge tube was evidence that atoms of different elements were all built up of one primary "matter in a new state," since the carriers were the same whatever the gas in the tube might be.

15. Positive Rays

The theory of gaseous ionization propounded in section 12 suggests that positive ions must be present in the discharge tube, formed by the removal of electrons from the atoms composing the residual gas. If this is the case, such ions must travel towards the cathode in the direction opposite to that of the cathode rays. Goldstein found that when a perforated cathode was used, certain rays passed through it, causing a glow in the tube. This luminosity was attributed to ionization of the molecules of gas in their path. The rays could also be detected by using a fluorescent screen of powdered willemite, which glowed with green light when struck by them. For permanent results, a photographic plate may be substituted in place of the screen. Wien found that the rays were deflected by a magnetic field in the opposite direction to that which would be observed in the case of cathode rays travelling in the same path. He concluded that they consisted of positively-charged particles, the stream constituting what is now generally known as "positive rays." Now a positive ion is a charged molecule of gas, so that it will possess mass of the same order of magnitude, and different values of the ratio e/m should be obtained when the gas in the tube is changed. Wien and Thomson subjected the rays to experiment, and values of e/m and the velocity v were obtained, in agreement with the above views.

Thomson applied electric and magnetic fields in the same direction. The direction of the deflected stream was, therefore, the resultant of two effects acting at right angles.[19] The rays were then received upon a photographic plate. Now the magnetic and electric displacements of a charged particle

moving under these conditions can be expressed in terms of e/m and v, the quantities desired, as follows :—

$$\frac{y}{x} = Av\frac{H}{X} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{y^2}{x} = B\frac{e}{m}\frac{H^2}{X} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where x, y are the co-ordinates of the deflected position (referred to the central undeflected position as origin) A, B are constants for a given apparatus, and H, X are the strengths of the magnetic and electric fields respectively. The plates on development showed that the positive rays were composite. Three simple types were enumerated by Thomson, as follows :—

1. The central spot in the position $x = y = 0$.

2. Straight lines passing through the origin, which correspond, according to equation (5), to rays having constant velocity, but variable e/m.

3. Parabolic arcs corresponding to rays having constant e/m, but variable velocity, in accordance with equation (6). It may be supposed that the differences in velocity are due to the fact that the positive ions are formed at varying distances from the cathode, so that different particles pass through different potential gradients. Considering a number of particles whose e/m ratio is the same, it follows, by (6) above, that $y^2 = kx$, where k is a constant for given fields, so that, instead of a single deflected spot, a parabolic curve is obtained. Another set of particles, which possess another value of the ratio e/m, will yield a second arc corresponding to $y^2 = k_1x$, where k_1 is another constant. In this way, it will be seen that the positive ray method can be used to sort out the particles, bringing all those which possess the same ratio of charge to mass to the same curve on the plate.

It is found necessary, in order to interpret the curves, to suppose that the charges of the particles composing the positive stream are variable. This is somewhat contrary to expectation, for it has been concluded above that in ionization singly charged positive ions only are produced. The conditions prevailing in the discharge tube thus appear to give rise to a somewhat exceptional state of affairs. According to this, in certain circumstances, more than one electron may be detached from the same atom. Further, the particles registering themselves on the photographic plate have not necessarily the same mass, even

when a pure gas is present in the tube. It appears that registration takes place so quickly that certain unstable combinations may be represented. For instance, using methane (CH_4), parabolas are formed which have been attributed to CH, CH_2 and CH_3. Thomson observed a parabola corresponding to H_3 in a gas obtained by bombarding caustic potash with cathode rays. If, then, both e and m can vary, the interpretation of the curves may be difficult. In general, however, the most deflected parabolas will correspond to the simplest cases. For if, according to equation (6) above, y^2/x is proportional to e/m, then for a given charge e, the smaller the mass m, the greater is the proportionality constant. Since the value of this constant is a measure of the *latus rectum* of the parabolic curve, the widest parabolas will, in general, correspond to the smallest masses. In the case of hydrogen, the outermost curve has been attributed to a hydrogen atom which is singly charged, i.e. which has lost one electron. The constants A and B for a given apparatus depend upon its dimensions and can be evaluated. In this way, it is found that the widest parabola in hydrogen does correspond to a value of e/m which is the same as that for the hydrogen ion in electrolysis. When the origin of one curve has been definitely decided, it is generally possible to determine the origin of others.

The constant velocity of the positive rays of type (2) was given by Thomson as 2×10^8 cms. per second, in a particular experiment.

16. Mass-Spectra and Isotopes

Prout's suggestion that elementary atoms were aggregations of hydrogen atoms, with atomic weights therefore expressible by whole numbers, has recently received special attention. By an application of the positive ray method, Aston proved that a basis of truth underlay this conception, although it had been completely abandoned for many years.

"Isotopes," elements with different atomic weights, closely resembling each other in chemical and physical properties, have been known for some time in the radioactive series of elements. Mixtures of these isotopes were very difficult to separate by ordinary methods. Further, it appeared that each member of a group of this kind should occupy the same square in the periodic classification. This will be further considered in section 29. Aston extended the idea to the non-radioactive elements, and showed that ordinary chlorine is composed of at least

two different "chlorines," which have atomic weights of 35 and 37. These varieties of chlorine, then, were isotopes, which closely resembled each other, although their atoms had different weights. The way in which positive rays were employed to establish these conclusions must now be considered.

Aston used a modification of Thomson's method, described in the preceding section, the electric and magnetic fields being applied successively at right angles to each other.[20] He succeeded in causing particles of the same mass to reach the same part of the receiving plate, a series of points or bands being obtained in place of the parabolas of Thomson. This was accomplished by making the mean deflection due to the electric field one-half of that due to the magnetic field. In these circumstances, there is a great increase in intensity, so that the time of exposure can be shortened. The full mathematical analysis which underlies the use of the "mass-spectrograph" has recently been given.[21] Fig. 8 shows the arrangement of the apparatus.

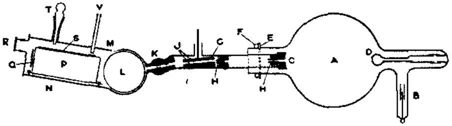
The interpretation of the results obtained by this method required considerable skill. The mass corresponding to a given line was determined by comparison with any known lines in the neighbourhood, for example, those of the previously-determined CH, CH_2 and CH_3. There were found to be, beside the direct spectrum of the "first order," spectra of higher orders corresponding to particles which had lost more than one electron. Thus a particle carrying three charges was indistinguishable from another carrying a single charge and possessing one-third of its mass, since the e/m ratio was the same in the two cases. In this way, it behaved as if it possessed an "effective" mass of one-third of its actual mass. For example, oxygen gives first and second order lines corresponding to masses 16 and 8, while the molecule gives a line of the first order corresponding to mass 32. The case of neon is of special interest from a historic point of view. In 1913, Thomson stated that he had found evidence of an element of atomic weight 22 when examining a sample of gas containing the rare gases of the atmosphere by the positive ray method. Now, doubly-charged carbon dioxide molecules ($\frac{1}{2}CO_2 = 22$) would possibly account for this result, but Thomson was able to show that this was not the true explanation. He passed the gas through tubes immersed in liquid air, and found that, while the line at 44 (corresponding to molecules of CO_2 with single charges) vanished, the 22 line persisted unchanged in intensity. Two possible explanations were suggested. The

line might be attributed to the presence of a compound NeH_2, or to an element similar to neon which occupied the same space in the periodic system, just as in another part of the table iron,

FIGURE VIII

MASS-SPECTROGRAPH (ASTON)

(*Phil. Mag.*, 1920; (vi) 39, 612)



A. Discharge tube, having anode at B and perforated concave aluminium cathode at C.
D. Silica bulb to prevent melting of the end of the tube by cathode rays.
E. Brass collar, for connection to brass tube G, cemented with wax to neck of bulb, cooled by water circulating through tube F.
H, H. Fine aluminium slits.
J. Parallel sloping brass plates for electric field, upper plate being connected to battery and the lower plate earthed.
K. Stopcock carrying a diaphragm. By rotating K, the beam may be stopped down. A second fixed diaphragm is placed between K and J.
L. Pole pieces of a large electromagnet, soldered into the brass tube M which carries the camera N.
P. Two vertical earthed brass plates.
Q. Willemite screen, which may be viewed through R.
S. Photographic plate, reached by beam through slot 2 mms. wide and 11·8 cms. long.
T. Torque rod, working in a ground glass joint, for moving plate into position.
V. Aperture for admission of light when desired.

The whole apparatus is evacuated by a Gaede mercury pump, the gas to be analysed being admitted through a side tube (not shown) behind the cathode. Two charcoal bulbs are attached and immersed in liquid air for some time before commencement of an experiment.

nickel and cobalt were grouped together. When Aston investigated neon, he found two lines of the first order, corresponding to atomic weights of 20 and 22. The intensity of the 20 line was greater than that of the 22 line, in accordance with the

accepted atomic weight of neon, namely 20·2. Many of the other elements have been investigated in a similar way. Of the first 18 elements of the periodic table, the following have been proved to be composite: lithium (6, 7), boron (10, 11), neon (20, 22), magnesium (24, 25, 26), silicon (28, 29), chlorine (35, 37) and argon (36, 40). The remaining elements have atomic weights which closely approximate to the whole numbers given after them in the following list: hydrogen (1), helium (4), beryllium (9), carbon (12), nitrogen (14), oxygen (16), fluorine (19), sodium (23), aluminium (27), phosphorus (31) and sulphur (32). Thus isotopes have been found for just those elements which do not possess integral atomic weights, and Prout's hypothesis has found some experimental foundation. There exists, however, one notable case which may be regarded as an exception. It has been pointed out that the atomic weight of hydrogen is 1·008 on the oxygen = 16 scale. Moreover, isotopes have not been detected in hydrogen and oxygen, and Aston claims an accuracy of 1 in 1000 for his results. This would seem to require further explanation, which will be found on page 159.

Further consideration of isotopes will be deferred to Chapter V. This discussion may be concluded for the present by noting that Dempster has elaborated an elegant method of positive ray analysis depending essentially on separation due to a magnetic field alone.[22]

17. X-Rays and the Elucidation of Crystal Structure

(A) *The Nature of X-Rays.*—It is proposed next to consider the third kind of rays present in the discharge tube, namely, those discovered by Röntgen in 1895, now generally known as "X-rays."[23]

It has been observed that X-rays are generated when cathode rays fall upon matter. If the cathode rays, emitted by a circular cathode, are brought to a focus where an "anticathode" of platinum or tungsten is placed, the X-rays can be obtained in adequate intensity for experimental investigation. The anticathode must be kept cool in some way, and this is conveniently accomplished by the circulation of cold water. The X-rays have much greater penetrating power than either of the two kinds of rays so far considered. (This is especially noticeable in high vacua, where exceptionally "hard" rays are produced.) They can pass readily through black paper and affect a photographic plate. Denser substances, such as bone, are compara-

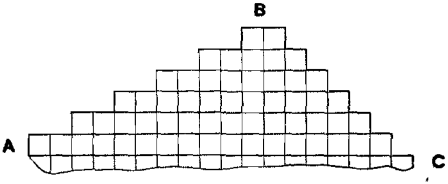
tively opaque. Thus an X-ray photograph of a hand shows the outline of the bones, and of any metallic object present, such as a gold ring. This considerable penetrative power is linked with the absence of deflection under the influence of applied electric or magnetic fields. Further, in common with light rays, X-rays have been found to exhibit the phenomena of scattering, diffraction, and interference. Their behaviour suggested to Stokes that they consisted of electromagnetic waves of higher frequency than those of light and heat.[24] Johnstone Stoney expressed the same opinion,[25] and this view was supported by the experiments of Blondlot and Semenoff.[26] Walter and Pohl, working on the diffraction of X-rays through fine slits, deduced that they had a possible wave-length of the order of 10^{-8} cm.[27] Their behaviour in relation to crystals explained below confirms the conclusion that they are "light" rays of short wave-length and high frequency, emitted when electrons travelling with high speed strike an obstacle, and that they are the result of the disturbance set up when the impact occurs. When they, in their turn, strike an obstacle, part of the beam is "scattered," and part of the energy reappears as the "characteristic" radiation of the struck atoms. Further, the impact of X-rays upon matter causes the emission of electrons moving with considerable velocities, known as "secondary beta rays." Lastly, perhaps entirely due to the latter effect, they produce ionization in gases, and cause the emission of both secondary and scattered X-rays.

(B) *X-Ray Methods of Investigating Crystal Structure.*—The regularities of crystals have always suggested that some regular internal arrangement existed. The method of growth of a crystal, the action of "etching" agents, the presence of regular inclusions and the existence of cleavage planes tended to support this conclusion. It is an interesting fact that Haüy enunciated his idea of the discontinuity of solid matter (based on a study of crystals) two years before Dalton proposed his atomic theory of matter. Haüy pictured a crystal as built up of small units, whose faces were parallel to the planes of cleavage. He described five types of symmetry for crystals, and the intervening years have only added one to this number. He also enunciated the "Law of Rational Indices," according to which the intercepts cut off by the faces on the "axes of symmetry" were in simple ratios. This had been previously suggested by Guglielmini, in 1705, but had been lost sight of during the century which followed. In order to explain faces which were not

parallel to the cleavages, Haüy supposed that the faces were "stepped" as shown in Fig. 9. It was, however, left to von Lang to establish the true nature of crystal symmetry. He showed that planes and axes of symmetry were involved, and divided crystals into 32 classes, grouping them into six large systems, namely, Triclinic, Monoclinic, Orthorhombic, Tetragonal, Hexagonal and Isometric (Cubic). Crystals of Class 1 possessed the lowest symmetry, and those of Class 32 the highest. The systems may also be grouped according to the effect of light upon the crystals in them. In 1819, Mitscherlich

FIGURE IX

HAÜY'S THEORY (1782)



The crossed lines indicate cleavage planes of a crystal. A B and B C appear as plane faces to an observer, the indentations being of molecular dimensions.

Haüy's conception (1) accounted for faces not parallel to the cleavage planes, and (2) explained Guglielmini's Law of Rational Indices.

made some important observations on crystals, and studied their "isomorphism," a name apparently suggested by Berzelius. The former pointed out that chemically related substances often possessed very similar external geometric forms. The term "*morphotropy*" was afterwards used by von Groth to express the similarity of chemical composition which often accompanies similarities in the axial ratios of a crystal. As an example, cited by von Groth, the following may be given :—

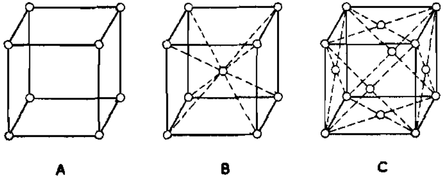
		Axial Ratios.
Metadinitrobenzene .	$C_6H_4(NO_2)_2$ . . .	$a : b : c = 0·943 : 1 : 0·538$
Trinitrobenzene . .	$C_6H_3(NO_2)_3$ . . .	$a : b : c = 0·954 : 1 : 0·733$

The crystallographers, Frankenheim and Bravais, investigated the number of ways in which space could be homogeneously partitioned. The result was embodied in the now familiar theory of the "space-lattice." For examples of such lattices, see Fig. 10. Consequent on these early labours and the later work of Sohncke, von Federow, Schonflies, and Barlow, the whole of the 32 systems of von Lang have been satisfactorily accounted for.[28] For this reason, crystallography is sometimes referred to as a "completed science."

In 1912, Friedrich and Knipping, working on the passage

FIGURE X

CRYSTAL LATTICES OF THE CUBIC SYSTEM



A. Simple Cubic Lattice.
B. Cube-centred (or Body-centred Cubic) Lattice.
C. Face-centred Lattice.

Crystal structures may be obtained by the continued repetition of a single elementary lattice in space, or by the interpenetration of one lattice system by another (*see* Fig. 14 and text).

of X-rays through crystals, obtained a "spot" diagram in accordance with the predictions of Laue, which were based on mathematical grounds.[29] It was found that rotation of the crystal produced a change in the pattern. If the rays were directed along an axis of four-fold symmetry, the pattern had four similar segments (as represented in Fig. 11) and when they travelled along an axis of three-fold symmetry, the spots were arranged in three similar segments. This showed quite clearly that the rays were in some way *reproducing the structure of the crystal*.

Laue attributed this result to diffraction, and stated that the

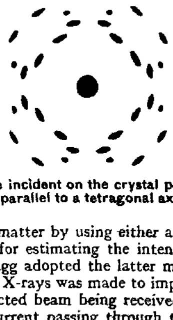
crystal behaved as a " raumgitter," or three dimensional grating. When the X-rays struck the crystal, each atom within it became the centre of a new disturbance. The resulting waves " interfered " in a manner familiar in the case of light. The spots were points of maximum reinforcement. The reason for this behaviour on the part of X-rays was attributed to their short wave-length, which was of the same order of magnitude as that of the distance between two adjacent atoms in a crystal.

Not long after the publication of the above work, W. L. Bragg made the important discovery that the layers of atoms in a crystal could be used as reflecting planes for X-rays which were incident at glancing angles.[30] It has been found possible

FIGURE XI

SPOT-PHOTOGRAPH OF ZINC BLENDE

(*Proc. Camb. Phil. Soc.*, 1914; 17, 56)



The X-rays were incident on the crystal perpendicular to a cube face, and parallel to a tetragonal axis of symmetry.

to investigate the matter by using either a photographic or a[n] ionization method for estimating the intensity of the reflecte[d] beam. W. H. Bragg adopted the latter method (see Fig. 12) A narrow pencil of X-rays was made to impinge on a surface o[f] a crystal, the reflected beam being received in an " ionizatio[n] chamber." The current passing through this chamber as th[e] crystal was turned was a measure of the intensity of the reflecte[d] rays. The original rays were fixed in direction, but both th[e] crystal and the ionization chamber could be turned, and for th[is] purpose were mounted on a table similar to that of a spectr[o]meter. As in the case of light, the angle moved through b[y] the reflected ray was always twice that moved through by th[e] incident ray, so the chamber was moved in such a way as

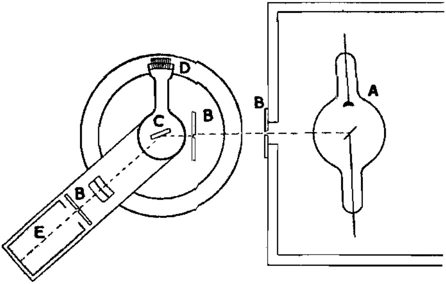
fulfil this condition. It was found that the current showed maximum values for certain angles of incidence. This was readily explained as the result of interference.[81]

A crystal, according to the lattice theory, contains atoms distributed in accordance with some regular elementary pattern which is repeated again and again in the three dimensions of

FIGURE XII

APPARATUS FOR CRYSTAL STRUCTURE
(W. H. and W. L. BRAGG)

(*Proc. Roy. Soc.*, 1913; A 88, 433)



A. X-ray bulb.
B, B, B. Adjustable lead slits.
C. Crystal.
D. Vernier for reading position of crystal.
E. Ionization chamber, filled with sulphur dioxide.

The crystal was mounted on a spectrometer table, the intensity of the reflected beam being measured for different angles of incidence of the X-rays, by means of the current passing through the ionization chamber.

space. When these arrangements are studied in detail, it is found that certain parallel sets of planes exist which are very thickly studded with atoms. It is reasonable to suppose that such planes will be specially efficient reflectors of X-rays. Let a beam of rays, consisting of one wave-length only (i.e., "monochromatic") be travelling in a fixed direction which is,

at the commencement of the experiment, parallel to the planes of a structure of this kind. If, now, the system is slowly turned to meet the rays, they will begin to fall on the planes at grazing incidence. As the wave-front passes over each atom in turn, a pulse will be set up similar in character to the original radiation. The forward portions of these pulses will combine to form a new wave-front, so that the planes may be treated as continuous, as in the case of the reflection of light at a plane surface. A small fraction of the energy of the wave will be reflected at the first plane, the remainder passing on to the second plane, where a portion will be reflected, and so on. Now, strong reinforcement of the reflected wave will occur if the waves reflected from different planes are in phase on emergence, and this will occur only for certain definite angles of incidence. At other angles, interference almost completely extinguishes the reflected beam. The condition for reinforcement may be readily proved to be—

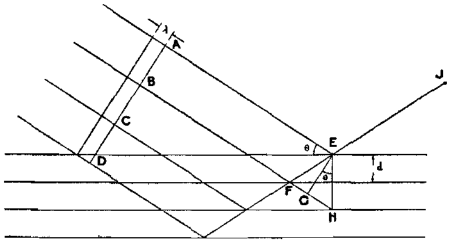
$$2d \,.\, \sin\theta = n\lambda \quad . \quad . \quad . \quad . \quad (7)$$

where d is the distance between the reflecting planes, θ the glancing angle of incidence, n a whole number, and λ the wave-length of the beam (Fig. 13). Thus, a series of positions of reinforcement will be obtained, which will be given by putting $n = 1, 2, 3, \ldots$ successively in the above relation. If the rays are not truly monochromatic, more than one series will be observed. For example, when a platinum anticathode is used in the X-ray bulb, three series of maxima are obtained, corresponding to three characteristic wave-lengths emitted by platinum. The first members of each series will correspond to the case $n = 1$, and constitute an X-ray spectrum of the first order. In this, reinforcement occurs between a ray reflected at the first plane of atoms, and rays reflected from the other planes, which differ from the first ray by just one whole wave-length. In a similar way, the second members correspond to the case $n = 2$, and form a spectrum of the second order, and so on. A series may be considered to correspond to a definite value of λ, whereas a spectrum is defined by the value of n. When the angles of incidence are plotted against the current passing through the ionization chamber, peaks occur on the curve for angles at which reinforcement takes place. The heights of these peaks afford a measure of the intensity of the reflected beam, and decrease as the order of spectrum increases.

(C) *Some Results of the X-Ray Methods*—(*a*) *Inorganic Crystals.*—In the case of *sodium chloride*, W. L. Bragg found that by directing the rays upon *a plane symmetrically placed* with regard to the three axes of symmetry, the intensities of the orders of spectra were of an alternating character, the odd orders being weak, and the even orders strong.[32] He explained this result by assuming that the reflecting planes in this case contained

FIGURE XIII

REFLECTION OF X-RAYS BY A CRYSTAL



A B C D represents a wave-front of X-rays, wave-length λ, incident on a crystal face at a glancing angle *θ*. The waves are reflected at successive parallel planes of the crystal, the planes being thickly studded with atoms. If path difference between A E J and B F J equals one whole wave-length λ, or any multiple of λ, reinforcement of the beam occurs along E J. *This difference is equal to* B H − A E = G H = $2d \sin\theta$. Hence, condition for reinforcement is $n\lambda = 2d \sin\theta$, where *n* is a whole number, and *d* is the distance between consecutive planes.

atoms of sodium and chlorine alternately. (Such planes are shown in outline in the structural diagram A of Fig. 14.) Thus the first plane might consist of atoms of chlorine only, and the second of atoms of sodium only, and so on. If the intensity of radiation scattered by an atom was roughly proportional to its atomic weight, the difference between that of sodium (23) and that of chlorine (35·5) would account for the observed result. In the case of *potassium chloride*, where the weights of

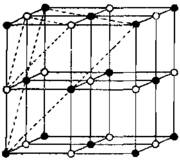
the atoms were more nearly equal (K = 39, Cl = 35·5), this difference of intensity was not observed. The *odd* orders of spectra (n = 1, 3 . . .) are practically extinguished, since the metal atom planes reflect waves of approximately equal intensity to those of the chlorine atom planes, but of opposite phase. With sodium chloride, however, the intensities of the waves from the two kinds of planes are unequal, so that, although the phases are opposite, extinction does not occur completely. The result is a feeble first order reflection, a strong second order reflection, a faint third order reflection, and so on, alternately. (These conclusions may be readily derived, from the study of a diagram similar to Fig. 13 on page 65, by considering the effect imposed by reflections from a set of planes half-way between that shown. It will be found that *extinction* of waves reflected by the original set of planes occurs in the case of the *odd* orders of spectra, while in the case of *even* orders reinforcement takes place.) With *potassium bromide* and *potassium iodide*, the relatively heavy bromine and iodine atoms tend to be responsible for all the reflection brought about by their crystals. (It will appear (section 27) that, as the atomic weight increases, the number of "extranuclear" electrons also increases. The scattering depends upon the number of these electrons, and indirectly upon the weight of the atom concerned.) The four substances mentioned above, denoted by NaCl, KCl, KBr and KI, belong to the cubic system, and W. L. Bragg proved that they possessed a cubic internal structure. He directed the same homogeneous X-radiation upon different faces of a rock salt crystal. According to equation (7) above, when $n = 1$, for a given value of λ, the distance d is inversely proportional to $\sin\theta$; or, in other words, the sine of the angle of incidence causing first order reinforcement on a face is inversely as the distance between the reflecting planes. Thus, measurement of the angles giving first order reinforcement in different directions enabled the *relative* distances between the reflecting planes of atoms to be determined. Bragg found that these relative distances corresponded with those demanded by geometrical considerations of the cubic arrangement shown in Fig. 14 (A), in each of the four cases mentioned above.[23] A study of this figure or of a model will show that a line which passes through the structure *symmetrically* with regard to the three edges which meet at a corner, that is, a *trigonal* axis of symmetry, is normal to planes consisting entirely of metal or entirely of halogen atoms alternately. If the X-rays are directed upon

FIGURE XIV

SOME CUBIC STRUCTURES

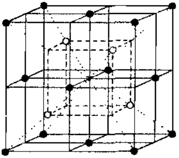
(*Proc. Roy. Soc.*, 1913; A 89, 284, 470, 474)

A ROCK SALT



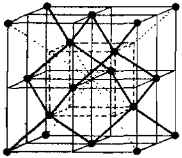
● Sodium
○ Chlorine

B ZINC BLENDE



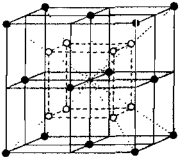
● Zinc
○ Sulphur

C DIAMOND



● Carbon

D. FLUORSPAR



● Calcium
○ Fluorine

The above structures are obtained by the interpenetration of simple cubic lattices. In A, B and C, each framework consists of two interpenetrating face-centred lattices; in D, the calcium ions are on a face-centred lattice, while the fluorine ions are on a simple cubic lattice (cf. Figure 10). When X-rays are directed towards a crystal face parallel with planes outlined in A above, the spectrum obtained corresponds with planes consisting entirely of sodium and chlorine ions alternately. •The diamond structure is shown from another point of view in Figure 15.

the face of a crystal parallel to such planes, the extinction effects mentioned above are observed. With other planes, such as those parallel to a cube face, the effect is absent, since the planes are alike, and contain both metal and halogen atoms in equal numbers.

The structure of a crystal of alkali chloride being determined, it is possible to measure the wave-length of a beam of X-rays. Consider an elementary cube of potassium chloride, of which eight may be supposed to be depicted in Fig. 14 (A). It has potassium atoms at four of its corners and chlorine atoms at the other four. Since any atom in the interior of a crystal of sylvine is at the junction of eight elementary cubes, it follows that only one-eighth of its mass is part of any one cube. In the elementary cube, therefore, there are four-eighths, or half an atom of potassium, and half an atom of chlorine, that is, half a molecule of potassium chloride. The corresponding mass can be calculated by multiplying half the molecular weight of sylvine by the mass of an atom of hydrogen. This elementary cube has thus a known mass M, which may be equated to ρd^3, where ρ is the density of sylvine and d the length of the edge of the cube, or elementary "lattice constant." From this, the value of d can be determined, and is found to be 3·13 A.U for sylvine, and 2·81 A.U. for rock salt (A.U. $= 10^{-8}$ cm.). If, now, the angle is determined for which first order reinforcement occurs with a crystal whose lattice dimensions are known, using X-rays of unknown wave-length, each of the quantities necessary to derive λ by means of the equation $\lambda = 2d \sin \theta$ is known. By applying this principle to the hardest rays emitted by a silver anticathode ("K" rays), the emission wave-length may be deduced as 0·56 A.U. It will be clear that, once the wave-length of rays characteristic of a given metallic anticathode is determined, such radiation can be applied in different directions to crystals whose lattice dimensions are required. An attempt may then be made to decide what space arrangement of the constituent atoms of the crystal is consistent with the experimental results, by geometrical considerations.[24]

It may be noted that, according to classical crystallography, every crystal lattice may be referred to an elementary parallelepiped, the lattice being the continued repetition of this figure in space. This is the crystal unit; it possesses all the properties of the crystal as a whole, and contains *the substance* of a small number of molecules.

The Braggs believe that the fundamental units in certain

crystals, such as those of the alkali halides, are *not atoms but ions*. Debye and Scherrer have advanced theoretical considerations from which they conclude that the intensity of radiation reflected by an atom depends primarily upon the number and position of the (extranuclear) electrons of an atom. Arguing from this, they deduce that a crystal of lithium fluoride consists of lithium and fluorine ions.[35] Born has arrived at similar conclusions, and, in conjunction with Landé, has attempted to link up the chemical and physical forces operating in an electropolar crystal in a quantitative manner.[36] It has been shown that the *compressibility* of a crystal is related to the potential energy set free when the ions, originally dispersed in space, come together to build up the crystal lattice. Born and Fajans have also applied the lattice theory with success to the calculation of the energy liberated when a halogen atom becomes an ion, the results being in satisfactory agreement with those deduced by independent methods.[37] It can, therefore, scarcely be doubted that the alkali halide crystal units are the ions of each kind. According to this view, in the potassium chloride structure, for example, every potassium ion is surrounded by six chlorine ions similarly placed with respect to it, and is held in position in the lattice by electrostatic forces. Similarly, every chlorine ion has six potassium ions, and the molecular identity of potassium chloride appears to be lost in the crystal.

It has been found, by X-ray analysis, that many of the more simply-constituted inorganic compounds crystallize according to one of the four following cubic types :—

1. *Sodium Chloride Type.*—In this case, *each* ion has *six* neighbours symmetrically grouped around it. All the *alkali halides* conform to this type, *except* those mentioned under type (2) below.[38] The following also belong to the group: *ammonium iodide* (at ordinary temperatures), *ammonium bromide* (above 137·8° C.), *ammonium chloride* (above 184·3° C.),[39] *silver chloride and silver bromide*,[40] the *oxides* of *magnesium, calcium* and *cadmium*, and probably *calcium sulphide*.[41] *Potassium cyanide* appears also to be strictly analogous.[42] The characteristic structure is that of two interpenetrating face-centred cubic lattices, arranged in such a way that every point of a simple cubic lattice is occupied by an ion (Fig. 14 (A)).

2. *Caesium Chloride Type.*—Here every ion has *eight* ions of the opposite kind symmetrically placed around it. Into this group fall *ammonium chloride* and *ammonium bromide* at ordinary temperatures,[39] *rubidium fluoride, caesium chloride, caesium*

bromide, caesium iodide[38] and *thallium chloride*.[43] The characteristic structure is that of the cube-centred (or "body-centred") cubic lattice (Fig. 10 (B)).

3. *Zinc Blende Type.*—In this group, every ion has *four* oppositely charged neighbours, symmetrically placed with regard to it. Besides *zinc blende* (ZnS),[38] *cuprous chloride, bromide* and *iodide* belong to the type.[44] The characteristic structure is that of two interpenetrating face-centred cubic lattices, placed in such a way that each small cube of Fig. 14 (A) has only four (alternate) corners occupied, each *alternate* cube having an ion at the centre (Fig. 14 (B)). The points occupied by ions form a pattern like that characteristic of the un-ionized *diamond* structure[45] (Fig. 15). The hardness of diamond corresponds with the rigidity of this framework. It may be difficult to realize that this structure, as depicted in the figure, has actually a cubic basis, but construction of a model on the lines explained above, and comparison with Fig. 14 (C) will show that this is so. It will also be seen that, in the case of zinc blende, the planes along a trigonal axis of symmetry consist alternately of zinc and sulphur atoms only, the distance separating the zinc atoms being four times that separating zinc and sulphur atoms. Moreover, the atomic weight of zinc being 65, and that of sulphur 32, extinction phenomena are noticed in the X-ray spectra from these planes, the second order spectra being almost extinguished by interference. The second order spectrum disappears in the case of diamond, where the atoms are of equal weight, as theory demands. The structure of diamond is in remarkable agreement with the well-known theories of van't Hoff and Le Bel, with regard to the symmetrical arrangement in space of four valency directions from the carbon atom.

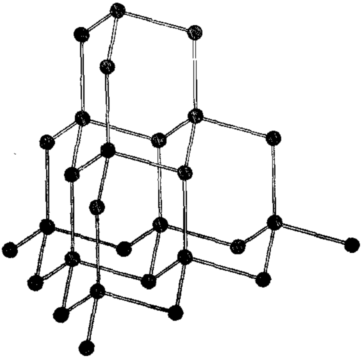
4. *Fluorspar Type.*—In *fluorspar*, CaF_2, the calcium ions are arranged in a face-centred cubic lattice, while the fluorine ions occupy the centres of the small cubes.[38] This type differs from Type (3), in that the centres of all the small cubes are occupied by fluorine ions, corresponding with twice as many fluorine atoms as calcium atoms in the compound (Fig. 14 (D)). Each calcium ion is surrounded by eight fluorine ions, and each fluorine ion is surrounded by four calcium ions. The *fluorides* of *strontium and barium* are believed to belong to this type. A somewhat similar case is afforded by *iron pyrites* (FeS_2), though it does not conform strictly to the group.[38] The iron atoms are on a face-centred cubic lattice, and each small cube contains a sulphur atom, which is, however, not at the centre of the cube.

The elementary metals are found to possess, for the most part, cubic or hexagonal structures. Thus *lithium*, *sodium*, *potassium*, *chromium*, *molybdenum*, *tantalum*, and *tungsten* have been assigned the cube-centred cubic arrangement; *copper*, *silver*, *gold*, *nickel*, *palladium*, *platinum*, *rhodium*, *iridium*,

FIGURE XV

STRUCTURE OF DIAMOND

(*Proc. Roy. Soc.*, 1913; A 89, 284)



Rings of six carbon atoms are linked together, in a way suggestive of the accepted structure of benzene. Each atom has four others symmetrically placed with regard to it, providing *tetrahedral symmetry, as in the models of Le Bel and van't Hoff.* The framework has a cubic basis (cf. Fig. 14 (c)).

aluminium, *calcium*, *lead* and *thorium* are arranged in a face-centred cubic lattice; while *zinc*, *cadmium*, *ruthenium*, *titanium*, *zirconium* and *osmium* are hexagonal, and *indium* is tetragonal (face-centred).[48]

In the structure of *ice*, the oxygen atoms are situated in the same way as the carbon atoms of diamond, with a hydrogen

atom midway in the line joining each pair of oxygen atoms.[47] Thus, each oxygen atom is surrounded by four hydrogen atoms symmetrically placed, and each hydrogen atom by two oxygen atoms. This leads to a particularly open structure, which offers an explanation of the fact that water expands on freezing, and accounts for the effect of pressure in melting ice. *Calcite*, so far as the calcium and carbon atoms are concerned, is structurally like rock salt, the cubic structure being, however, deformed into rhombohedral arrangement corresponding with the natural cleavages.[32] The oxygen atoms lie on the lines joining carbon atoms. *Dolomite* and *sodium nitrate* have strictly analogous structures,[48] but *aragonite*, as would be anticipated, is different.[49] For further details concerning inorganic substances, the original memoirs must be consulted. A complete list of references to the end of 1923 is given in Wyckoff's book "The Structure of Crystals" (American Chemical Society's Monographs).

(*b*) *Organic Crystals.*—A new field has been opened up by the application of the X-ray method to organic crystals, many of which are monoclinic, the unit cell being a rectangular parallelepiped deformed so that one angle is oblique. The monoclinic system of crystals may be referred to three unequal axes, one of which is perpendicular to the other two. It appears, from comparison of X-ray measurements with the diameters of the atoms concerned, that organic crystals are characterized by the fact that the molecule, or a group of molecules, forms the basis of the various structures. They differ fundamentally from the inorganic salts, where ions are united electrostatically, and where it is impossible to recognize the molecule. The forces which unite the molecules together in organic crystals are presumably weaker than the electrostatic forces in inorganic crystals, so that the melting-points of organic crystals are generally low. On the other hand, the valency forces prevailing within the organic molecules are stronger than the forces between molecules, and the molecule is preserved on melting. Another characteristic of the structures of organic crystals is the openness of the arrangements, which results in low density. The diamond spacing (cubic) is very open, and this arrangement is apparently present in aliphatic crystals. The *graphite* arrangement (trigonal), where one of the four bonds of carbon in diamond has been weakened, so that the atoms are arranged in hexagonal rings in layers,[50] may be supposed to form the basis of the aromatic crystals. A single hexagonal ring may correspond

with the benzene structure, and two rings with the naphthalene structure. If, as seems probable, these rings have definite form and size, and are very little altered by substitution, the problem, as regards the aromatic crystals, is simplified considerably.

The unit cell of *naphthalene* has been found to contain the substance of two molecules.[51] If one molecule is placed at each of the eight corners of the cell, this corresponds with one molecule in the elementary cell. The second molecule is accounted for by the necessity of placing two molecules at the centres of two opposite faces, thus contributing two half molecules, that is, another molecule to the cell. Evidence based on the absorption spectrum of naphthalene vapour indicates that the carbon atoms are nearer together in naphthalene than in diamond.[52] A similar arrangement is assigned to *anthracene*.[53] The absolute dimensions of the unit cells of naphthalene and allied substances have been determined, and are here given in Ångstrom units, together with the oblique angles, in the following cases :—

	a.	*b*.	*c*.	*β*.
Naphthalene	8·34	6·05	8·69	122° 49′
Anthracene	8·58	6·02	11·18	125° 0′
α-naphthol	13·1	4·9	13·4	117° 10′
β-naphthol	11·7	4·28	17·4	119° 48′
Naphthalene tetrachloride	8·05	10·5	7·35	112° 26′

It is found that, in naphthalene, the β-hydrogen atoms of one molecule lie adjacent to the corresponding atoms of another molecule, while the α-hydrogen atoms adjoin the carbon atoms of neighbouring molecules. The forces which unite the β-hydrogen atoms of one molecule to the next appear to be weak, and the points of contact constitute the cleavage plane of naphthalene. Passing from naphthalene to anthracene, it will be seen that the addition of another ring increases the length of the *c* axis by 2·5 A.U., which is about the calculated amount for a benzene ring. With α- and β-naphthol, the axial lengths are increased, but here four molecules enter into the unit cell.[51] When the hydroxyl group is moved from the α to the β position, the *a* and *b* axes are shortened, and the *c* axis is considerably lengthened. The increase in length, measured along the direction in which the molecule is supposed to lie, is about equal to

*the diameter of an oxygen atom. With naphthalene tetra*chloride, the *b* axis is elongated, as compared with naphthalene, the increase of 4·0 A.U. corresponding approximately to twice the diameter of the chlorine atom. The compound is considered to be produced by the attachment of the four chlorine atoms, in two groups of two each, to opposite sides of the naphthalene molecule. In this way, the width of the molecule is increased by the measured amount.

Astbury has investigated the case of *tartaric acid*, as well as the optically-inactive *racemic acid* (molecular compound of the left- and right-handed forms).[54] The results are in remarkably good agreement with the conclusions of Pasteur and later workers. It is found that the carbon atoms in tartaric acid are arranged spirally, and it is suggested that this is associated with its optical activity.

Müller and Shearer have conducted important experiments on the X-ray spectra of *long-chain aliphatic compounds*. The substance is melted on to a glass plate or strip of mica (which gives convenient reference lines) and turned to meet the rays on a spectrometer table in the usual manner. Müller obtains well-defined lines of the various orders of reflection using the fatty acids.[55] These lines approach each other more nearly as the molecular weight of the acid used increases, showing that the distances measured also increase (since d varies inversely as $\sin \theta$ for a given order of spectrum). It is shown that the increase in distance is 2·0 A.U. per CH_2 group added. This is actually greater than the accepted diameter of the carbon atom (1·5 A.U.), and it is, therefore, concluded that two molecules of acid are present between consecutive planes. Shearer has *confirmed that the addition of CH_2 to the acid part of a fatty* ester causes an increment in length of 1·0 A.U.[56] The following figures may be quoted (see p. 75). The distance d is in A.U., and is that between the planes measured.

From Shearer's results, the differing effects of adding CH_2 to the acid or to the ester part of a long chain is made clear. Between No. 7 and No. 10, 15 CH_2 groups are added to the ester group, and the increase in d per CH_2 group, is $(40{\cdot}4 - 22{\cdot}0)/15 = 1{\cdot}22$ A.U. Comparing No. 7 with No. 11, or No. 8 with No. 12, however, the difference, per CH_2 group added to the acid part of the chain, is 1·0 A.U. Different arrangements of carbon atoms must, therefore, be attributed to the two cases, and suggestions with regard to this have been made by Müller and Shearer in a joint paper.[57] The results

Substance.	Formula.	d.	
1. *Capric acid* .	$C_9H_{19}COOH$	23·2	Müller.
2. Lauric acid .	$C_{11}H_{23}COOH$	27·0	
3. Myristic acid .	$C_{13}H_{27}COOH$	32·2	
4. Palmitic acid .	$C_{15}H_{31}COOH$	34·7	
5. Stearic acid .	$C_{17}H_{35}COOH$	38·7	
6. Behenic acid .	$C_{21}H_{43}COOH$	47·8	
7. Methyl palmitate	$C_{15}H_{31}COOCH_3$	22·0	Shearer.
8. Ethyl palmitate .	$C_{15}H_{31}COOC_2H_5$	23·2	
9. Octyl palmitate .	$C_{15}H_{31}COOC_8H_{17}$	30·4	
10. Cetyl palmitate .	$C_{15}H_{31}COOC_{16}H_{33}$	40·4	
11. Methyl stearate .	$C_{17}H_{35}COOCH_3$	24·0	
12. Ethyl stearate .	$C_{17}H_{35}COOC_2H_5$	25·2	

appear to be consistent with the interpretation that the ester molecules are placed with their long axes normal to the planes, side by side, in a regular manner, as in the monomolecular films of organic substances on water of Langmuir.[58] These films have been systematically investigated, and the sizes of the molecules in them measured by Adam.[59] Two molecules, however, are grouped together in the case of the fatty acids, probably with their carboxyl groups in contact. It is worthy of note that two other spectral lines are found for the above substances, which are in the same positions in all cases, and this is attributed to constancy of cross-section of the various molecules, the length only being changed in passing from one compound to another. Piper and Grindley have conducted independent investigations with the sodium salts of fatty acids, and find the increase in length of molecule, per CH_2 group, to be 1·25 A.U.[60]

It has only been possible to consider the leading results which have been obtained by the X-ray method of studying crystals. Its special value lies in that not only does the angle producing a line give information as to the distance between similar planes in a given direction, but also the method enables the intensity of the reflected radiation to be measured, with important results. Interpretation is generally assisted by a study of Laue diagrams. The reader is referred to the Braggs' book, "X-Rays and Crystal Structure" (No. 15 in the Bibliographical list at the end of this book) for further information, as well as to the original literature.

The work of W. L. Bragg on the electron distribution in certain atoms is mentioned in section 56, and the Law of Atomic

Diameters receives attention in sections 44 and 52. The X-ray method has led to values of the diameters of atoms, on the assumption that in a crystal the atoms touch each other, in general conformity with those obtained by other methods.

It is now possible to apply X-rays to the problem of crystal structure, even when the substance under investigation is only available in powder form.[61] When a fine beam of X-rays is passed through a mass of finely-powdered matter, a certain number of crystals will happen to be so placed that reflection takes place. Since the particles may be orientated in any direction, the reflected beams will lie on the surfaces of cones, and appear as haloes on the photographic plate. A number of substances have already been examined, and some which were previously thought to be amorphous have been proved to be crystalline. Many of the results mentioned above have been obtained or confirmed by this method; as, for example, in the case of graphite. Solid argon at 40° absolute has been found to have the face-centred cubic lattice.[62]

Darwin has studied the reflection of X-rays by crystals from the mathematical point of view.[63] The necessary data for examination of each of the 230 groups of crystals has also been tabulated.[64]

A discussion of the nature of secondary X-rays and the characteristic X-rays of the elements is postponed to section 27, where Moseley's work on high frequency spectra is considered, in relation to the electronic theory of matter.

REFERENCES: (III)

See Nos. 2, 3, 4, 8, and 15 in Bibliographical List at end of book.

1 (p. 41) C. T. R. Wilson: "On the Leakage of Electricity through dust-free Air"; *Proc. Camb. Phil. Soc.*, 1902; **11**, 32.

2 (p. 41) J. J. Thomson and E. Rutherford: "On the Passage of Electricity through Gases exposed to Röntgen Rays"; *Phil. Mag.*, 1896; (v.) **42**, 392.

3 (p. 42) J. J. Thomson: "The Connection between Chemical Combination and the Discharge of Electricity through Gases"; *Brit. Ass. Rep.*, 1894, 482.

4 (p. 43) E. Rutherford: "The Velocity and Rate of Combination of the Ions of Gases exposed to Röntgen Radiation"; *Phil. Mag.*, 1897; (v.) **44**, 422.

5 (p. 44) J. Zeleny: "The Velocity of Ions produced in Gases by Röntgen Rays"; *Phil. Trans.*, 1901; **A195**, 193.

6 (p. 44) P. Langevin: "Recombinaison et mobilités des ions dans les gaz"; *Ann. Chim. Phys.*, 1903; (vii.) **28**, 485.

7 (p. 46) J. S. TOWNSEND: "The Diffusion of Ions into Gases"; *Phil. Trans.*, 1900; **A193**, 129.
8 (p. 47) *Idem*: "The Charges on Positive and Negative Ions in Gases"; *Proc. Roy. Soc.*, 1908; **A80**, 207.
9 (p. 47) E. M. WELLISCH: "The Motion of Ions and Electrons through Gases"; *Phil. Mag.*, 1917; (vi.) **34**, 33. See also *Amer. J. Sci.*, 1915; **39**, 583, and L. B. LOEB: *Phys. Rev.*, 1916; **8**, 633.
10 (p. 49) P. LANGEVIN: "L'ionization des gaz"; *Ann. Chim. Phys.*, 1903; (vii.) **28**, 289.
11 (p. 49) W. CROOKES: "On the Illumination of Lines of Molecular Pressure, and the Trajectory of Molecules"; *Phil. Trans.*, 1879; **170**, 135.
Idem: "Contributions to Molecular Physics in High Vacua"; *ibid.*, 641.
Idem: "On a Fourth State of Matter"; *Proc. Roy. Soc.*, 1880; **30**, 469.
12 (p. 50) A. SCHUSTER: "The Discharge of Electricity through Gases"; *Proc. Roy. Soc.*, 1889; **47**, 526.
13 (p. 50) P. LENARD: "Ueber Kathodenstrahlen in Gasen von atmos phärischem Druck und im äussersten Vacuum"; *Wied. Ann.*, 1894; **51**, 225: **52**, 23.
14 (p. 50) W. WIEN: "Untersuchung über die electrische Entladung in verdünnten Gasen"; *Wied. Ann.*, 1898; **65**, 440.
15 (p. 51) J. PERRIN: "Nouvelles propriétés des rayons cathodiques"; *Compt. Rend.*, 1895; **121**, 1130.
16 (p. 51) P. LENARD: "Ueber die electrische Wirkung der Kathodenstrahlen auf atmosphärische Luft"; *Wied. Ann.*, 1897; **63**, 253. See also *Ann. Physik*, 1903; (iv.) **12**, 449, 714: 1904; (iv.) **15**, 485.
17 (p. 51) J. J. THOMSON: "Cathode Rays"; *Phil. Mag.*, 1897; (v.) **44**, 298.
18 (p. 53) S. RATNER: "Experiments on the Nature of the Discharge of Electricity through Rarified Gases"; *Phil. Mag.*, 1920; (vi.) **40**, 785.
19 (p. 53) J. J. THOMSON: "Positive Electricity"; *Phil. Mag.*, 1909; (vi.) **18**, 821.
Idem: "Rays of Positive Electricity"; *Phil. Mag.*, 1910; (vi.) **20**, 752: 1911; (vi.) **21**, 225.
Idem: "Further Experiments on Positive Rays"; *Phil. Mag.*, 1912; (vi.) **24**, 209.
20 (p. 56) F. W. ASTON: "A Positive Ray Spectrograph"; *Phil. Mag.*, 1919; (vi.) **38**, 707. See references at No. 34, Chapter V.
21 (p. 56) F. W. ASTON and R. H. FOWLER: "Some Problems of the Mass Spectrograph"; *Phil. Mag.*, 1922; (vi.) **43**, 514.
22 (p. 58) A. J. DEMPSTER: "A New Method of Positive Ray Analysis"; *Phys. Rev.*, 1918; (ii.) **11**, 316. For application of this method see: *Ibid.*, 1921; (ii.) **18**, 415: 1922; (ii.) **20**, 631.
23 (p. 58) W. C. RÖNTGEN: "Ueber eine neue Art von Strahlen"; *Wied. Ann.*, 1898; **64**, 1.
24 (p. 59) G. G. STOKES: "On the Nature of the Röntgen Rays"; *Proc. Camb. Phil. Soc.*, 1898; **9**, 215.
25 (p. 59) G. JOHNSTONE STONEY: "Evidence that Röntgen Rays are Ordinary Light"; *Phil. Mag.*, 1898; (v.) **45**, 532.
26 (p. 59) R. BLONDLOT: "Sur la vitesse de propagation des rayons X"; *Compt. Rend.*, 1902; **135**, 666, 721, 763.

26 (p. 59) J. SEMENOW : " Sur la nature des rayons X " ; *Compt. Rend.*, 1901 ; **133**, 217.
27 (p. 59) B. WALTER and R. POHL : " Zur Frage der Beugung der Röntgenstrahlen " ; *Ann. Physik*, 1908 ; (iv.) **25**, 715. See also :—
A. SOMMERFELD : " Über die Beugung der Röntgenstrahlen " ; *Ann. Physik*, 1912 ; (iv.) **38**, 473.
28 (p. 61) A. E. H. TUTTON : " The Seven Styles of Crystal Architecture " ; *Brit. Ass. Rep.*, 1909 ; 736.
Idem : " The Structure of Crystals " ; *Brit Ass. Rep.*, 1901 ; 297.
29 (p. 61) W. FRIEDRICH, P. KNIPPING and M. LAUE : " Interferenzerscheinungen bei Röntgenstrahlen " ; *Ann. Physik*, 1913 ; (iv.) **41**, 971.
30 (p. 62) W. L. BRAGG : " The Specular Reflection of X-rays " ; *Nature*, 1912 ; **90**, 410. See also *Proc. Camb. Phil. Soc*, 1912 ; **17**, 43.
31 (p. 63) W. H. BRAGG and W. L. BRAGG : " The Reflection of X-rays by Crystals " ; *Proc. Roy. Soc.*, 1913 ; **A88**, 428 : **A89**, 246.
W. H. BRAGG : " X-rays and Crystal Structure " ; *Phil. Trans.*, 1915 ; **109**, 252.
32 (p. 65) W. L. BRAGG : " The Analysis of Crystals by the X-ray Spectrometer " ; *Proc. Roy. Soc.*, 1913 ; **A89**, 468.
33 (p. 66) *Idem* : " The Structure of Some Crystals as Indicated by their Diffraction of X-rays " ; *Proc. Roy. Soc.*, 1913 ; **A89**, 248.
34 (p. 68) W. H. BRAGG : " The Recent Work on X-rays and Crystals, and its Bearing on Chemistry " ; *J. Chem. Soc., Trans.*, 1916 ; **109**, 252.
Idem : " The Significance of Crystal Structure " ; *J. Chem. Soc., Trans.*, 1922 ; **121**, 2766.
Idem : " The Analysis of Crystal Structure by X-rays " ; *Brit. Ass. Rep.*, Presidential Address, Section A : 1924 ; 34.
A. E. H. TUTTON : " Ten Years of X-ray Crystal Analysis " ; *Nature*, 1922 ; **110**, 47.
35 (p. 69) P. DEBYE and P. SCHERRER : " Atombau " ; *Phys. Z.*, 1918 ; **19**, 474.
36 (p. 69) M. BORN : " Über die elektrische Natur der Kohäsionskräfte fester Körper " ; *Verh. Deut. Phys. Ges.*, 1919 ; **21**, 533.
M. BORN and A. LANDÉ : " Über die Berechnung der Kompressibilität regularer Kristalle aus der Gittertheorie " ; *Verh. Deut. Phys. Ges.*, 1918 ; **20**, 210.
37 (p. 69) M. BORN : " Die Elektronenaffinität der Halogenatome " ; *Verh. Deut. Phys. Ges.*, 1919 ; **21**, 679.
K. FAJANS : " Die Elektronenaffinität der Halogenatome, und die Ionisierungsarbeit der Halogenwasserstoffe " ; *Verh. Deut. Phys. Ges.*, 1919 ; **21**, 714.
8 (p. 69) W. P. DAVEY : " Precision Measurements of Crystals of the Alkali Halides " ; *Phys. Rev.*, 1923 ; (ii.) **21**, 143.
9 (p. 69) G. BARTLETT and I. LANGMUIR : " Crystal Structures of the Ammonium Halides above and below the Transition Temperatures " ; *J. Amer. Chem. Soc*, 1921 ; **43**, 84.
L. VEGARD : " Results of Crystal Analysis. IV." (NH_4I) ; *Phil. Mag.*, 1917 ; (vi.) **33**, 395.
R. W. G. WYCKOFF : " On the Crystal Structure of Ammonium Chloride " ; *Amer. J. Sci.*, 1922 ; (v.) **4**, 469.
) (p. 69) R. B. WILSEY : " The Crystal Structure of the Silver Halides " *Phil. Mag.*, 1921 ; (vi.) **42**, 262.

41 (p. 69) R. W. G. WYCKOFF: "The Crystal Structure of Magnesium Oxide"; *Amer. J. Sci.*, 1921; (v.) **1**, 138.
P. SCHERRER: "Das Raumgitter des Kadmiumoxyds"; *Z. für Kristallographie*, 1922; **57**, 186.
W. P. DAVEY: "Precision Measurements of the Crystalline Structure of Calcium Oxide, Calcium Sulphide and Calcium Selenide"; *Phys. Rev.*, 1923; (ii.) **21**, 213.
42 (p. 69) R. M. BOZORTH: "The Crystal Structure of Potassium Cyanide"; *J. Amer. Chem. Soc.*, 1922; **44**, 317. See also P. A. COOPER: *Nature*, 1921; **107**, 745.
43 (p. 70) W. P. DAVEY and F. G. WICK: "The Crystal Structure of Two Rare Halogen Salts" (CsCl, TlCl); *Phys. Rev.*, 1921; (ii.) **17**, 403.
44 (p. 70) R. W. G. WYCKOFF and E. POSNJAK: "The Crystal Structures of the Cuprous Halides"; *J. Amer. Chem. Soc.*, 1922; **44**, 30.
45 (p. 70) W. H. BRAGG and W. L. BRAGG: "The Structure of the Diamond"; *Proc. Roy. Soc.*, 1913; **A89**, 277.
46 (p. 71) A. W. HULL: Li, Na, K, Al; *Phys. Rev.*, 1917; (ii.) **10**, 661.
Idem: Cr, Mo, Ta, Ni, Pd, Pt, Rh, Ir, Co, Zn, Cd, Ru, In; *Phys. Rev.*, 1921; (ii.) **17**, 571.
P. DEBYE: "Die Atomanordnung von Wolfram"; *Phys. Z.*, 1917; **18**, 483.
W. L. BRAGG: "The Crystalline Structure of Copper"; *Phil. Mag.*, 1914; (vi.) **28**, 355.
L. VEGARD: "The Structure of Silver Crystals"; *Phil. Mag.*, 1916; (vi.) **31**, 83.
Idem: Pb, Au; *Phil. Mag.*, 1916; (vi.) **32**, 65.
A. W. HULL: "The Crystal Structure of Calcium"; *Phys. Rev.*, 1921; (ii.) **17**, 42.
Idem: "Crystal Structure of Titanium, Zirconium, Cerium, Thorium and Osmium"; *Phys. Rev.*, 1921; (ii.) **18**, 88.
47 (p. 72) W. H. BRAGG: "The Crystal Structure of Ice"; *Proc. Phys. Soc.*, 1922; **34**, 98. See also A. ST. JOHN: *Proc. Nat. Acad. Sci.*, 1918; **4**, 193 and D. M. DENNISON: *Phys. Rev.*, 1921; (ii.) **17**, 20.
48 (p. 72) R. W. G. WYCKOFF: "The Crystal Structure of some Carbonates of the Calcite Group"; *Amer. J. Sci.*, 1920; (iv.) **50**, 317.
Idem: "The Crystal Structure of Sodium Nitrate"; *Phys. Rev.*, 1920; (ii.) **16**, 149.
49 (p. 72) W. L. BRAGG: "The Structure of Aragonite"; *Proc. Roy. Soc.*, 1924; **A105**, 16, 370.
50 (p. 72) J. D. BERNAL: "The Structure of Graphite"; *Proc. Roy. Soc.*, 1924; **A106**, 749. See also papers at Ref. No. 61.
51 (p. 73) W. H. BRAGG: "The Structure of Organic Crystals"; *Proc. Phys. Soc.*, 1921; **34**, 33: *Nature*, 1922; **110**, 115.
52 (p. 73) V. HENRI and H. DE LÁSZLÓ: "The Analysis of the Absorption Spectrum of Naphthalene Vapour—Structure and Activation of the Molecule of Naphthalene"; *Proc. Roy. Soc.*, 1924; **A105**, 662.
53 (p. 73) W. H. BRAGG: "The Crystalline Structure of Anthracene"; *Proc. Phys. Soc.*, 1923; **35**, 167.
54 (p. 74) W. T. ASTBURY: "The Crystalline Structure and Properties of Tartaric Acid"; *Proc. Roy. Soc.*, 1922; **A102**, 506.
Idem: "The Crystalline Structure of Anhydrous Racemic Acid"; *Proc. Roy. Soc.*, 1923; **A104**, 219.

55 (p. 74) A. Müller: "The X-ray Investigation of Fatty Acids"; *J. Chem. Soc. Trans.*, 1923; **123**, 2043.

56 (p. 74) G. Shearer: "An X-ray Investigation of Certain Organic Esters and other Long Chain Compounds"; *J. Chem. Soc., Trans.*, 1923; **123**, 3152.

57 (p. 74) A. Müller and G. Shearer: "Further X-ray Measurements of Long Chain Compounds and a Note on their Interpretation"; *J. Chem. Soc., Trans.*, 1923; **123**, 3156.

58 (p. 75) I. Langmuir: "The Shapes of Group Molecules from the Surfaces of Liquids"; *Proc. Nat. Acad. Sci.*, 1917; **3**, 251. See also *Idem: J. Amer. Chem. Soc.*, 1917; **39**, 1868.

59 (p. 75) N. K. Adam: "The Properties and Molecular Structure of Thin Films on Water"; *Proc. Roy. Soc.*, 1921; **A99**, 336: 1922; **A101**, 452, 516: 1923; **A103**, 676, 687: 1924; **A106**, 694.

60 (p. 75) S. H. Piper and E. N. Grindley: "The Fine Structure of some Sodium Salts of Fatty Acids in Soap Curds"; *Proc. Phys. Soc.*, 1923; **35**, 269.

61 (p. 76) P. Debye and P. Scherrer: "Interferenzen an regellos orientierten Teilchen im Röntgenlicht"; *Phys. Z.*, 1916; **17**, 277: 1917; **18**, 291.

A. W. Hull: "A New Method of X-ray Crystal Analysis"; *Phys. Rev.*, 1917; (ii.) **10**, 661. See also *J. Amer. Chem. Soc.*, 1919; **41**, 1168.

62 (p. 76) F. Simon and Clara V. Simson: "Die Kristallstruktur des Argons"; *Z. Physik*, 1924; **25**, 160.

63 (p. 76) C. G. Darwin: "Röntgen Ray Reflexion"; *Phil. Mag.*, 1914; (vi.) **27**, 315, 675. See also *Phil. Mag.*, 1922; (vi.) **43**, 800.

64 (p. 76) W. T. Astbury and (Miss) K. Yardley: "Tabulated Data for the Examination of the 230 Space-Groups by Homogeneous X-rays"; *Phil. Trans.*, 1924; **A224**, 221.

CHAPTER IV

RADIOACTIVITY

18. The Nature of Radioactive Change

RÖNTGEN discovered X-rays in 1895, before radioactivity was known. In the following year, H. Becquerel [1] and S. P. Thompson,[2] working independently, found that a salt of uranium affected a photographic plate. This property was also found to be characteristic of certain minerals; for example, it was exhibited by pitchblende, which contained uranium. In 1898, P. Curie and Madame Curie succeeded in isolating a compound of a new substance from this mineral by a process of fractional crystallization.[3] This substance was named "radium," and was found to exhibit the properties which are associated with "radioactivity" in a marked degree. Demarçay confirmed the existence of a new element by spectroscopic evidence.[4] The compounds of radium affected a photographic plate very readily; they produced ionization in the air in their neighbourhood; they emitted rays continuously and spontaneously; they evolved light and heat and could promote certain chemical and physical changes.[1,5,6] In suitable circumstances, the compounds of radium gave rise to the same characteristic line spectrum, indicating that they had a common elementary constituent. Radium, then, appeared to be an element, whose salts were found to be isomorphous with the corresponding salts of barium. It was thus considered to be a member of the group of alkaline earths. It was found possible to determine its equivalent weight by conversion of the chloride into silver chloride.[7] The valency of radium being taken as equal to 2 from its similarity to barium, its atomic weight appeared to be about 226, and it thus found a place at the foot of the second group in the ordinary periodic classification of the elements. Radium, therefore, appeared, on the one hand, as a metal akin to calcium and barium, and, on the other, as a

substance capable of the spontaneous emission of rays, in a manner previously unobserved. Other substances were afterwards isolated which behaved in a similar way.

A careful examination of the rays emitted by radioactive materials showed them to be composite in character. Part of the radiation was distinguished from the remainder in being deflected by electric [8] and magnetic [9] fields. That this part was also composite was proved by the fact that deflections in opposite directions were observed. Some rays were deflected in a direction which would be consistent with the assumption that they consisted of a stream of positively-charged particles, while others were deviated to a greater extent in the opposite direction, which might be interpreted as showing that they consisted of a stream of light negatively charged particles. These deviations may be conveniently studied by application of suitable fields, a screen painted with barium platinocyanide or zinc sulphide being placed in the path of the rays, the position of the deflected beam being rendered visible by the light emitted where it strikes the screen. The first of the two types of rays mentioned above is known as "α-rays," and the second as "β-rays." The undeflected radiation, termed "γ-rays," is further distinguished by superior penetrating power towards matter.[10] The γ-rays can pass readily through half a centimetre thickness of lead, which easily stops the other kinds. The β-rays can pass through one-tenth of a millimetre thickness of aluminium, which will stop the α-rays. Thus it is possible to separate these rays, and study the behaviour of one variety acting alone. It was shown in this way that the β-radiation was mainly responsible for the photographic effect.

The quantitative study of the rays of radium and allied substances must now be considered.[11] Their property of inducing ionization of gases, with consequent increase in conductivity was utilized in order to examine their rates of emission. A solid radioactive substance was placed upon one electrode of an ionization chamber, this electrode being connected to a series of cells to give it a sufficiently high potential. The other electrode was placed parallel to the first and connected to opposite quadrants of an electrometer. The arrangement is shown in Fig. 16. The radioactive substance was covered as required with suitable screens to cut off all radiations, but those whose investigation was desired. The "saturation" current indicated by the electrometer was a measure of the degree of ionization of the gas between the electrodes, and,

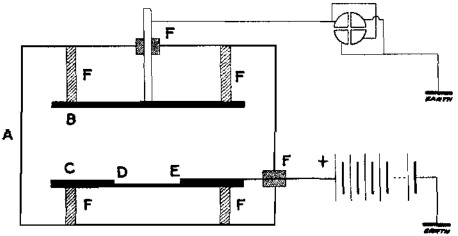
therefore, of the rate at which rays were being emitted. If the radioactive substance was a gas at the ordinary temperature, the apparatus was suitably modified, the principle involved being the same.

In 1900, Crookes observed that a residue could be separated from an uranium salt by chemical means, which appeared to have all the photographic activity of the original salt concen-

FIGURE XVI

APPARATUS FOR RADIOACTIVE RAYS (RUTHERFORD)

(*Phil. Mag.*, 1900; (v) 49, 162)



A Lead vessel, having a door at the side, through which the plate C may be inserted or removed.
B, C. Plates on insulating supports F, F. The plate C is charged by the battery, and B is connected to an electrometer.
D E. Small square depression in plate C, in which radioactive substance placed, with suitable coverings.
The rate of movement of the electrometer needle is a measure of the ionization current between the plates, which is proportional to the activity of the preparation.

trated in it.[19] He gave this residue the name uranium X. It could be prepared by adding excess of ammonium carbonate to the solution of the uranium salt until the precipitate first formed redissolved, leaving only a residue of uranium X, which could be separated by mechanical means, or it could be extracted from an aqueous solution of an uranium salt by means of ether. Now, the remarkable fact that some change occurred in both the

original salt and in the separated uranium X was soon observed. The latter, although it appeared to possess all the original photographic activity (due to β-rays) immediately after separation, gradually lost its activity, and the original salt gradually regained it, so that after six months the activity of the uranium was practically restored. At the end of this period, a further quantity of uranium X could be prepared, and the same changes were repeated. It therefore seemed clear that uranium was continually producing uranium X, and that this substance was responsible for the β-ray activity. The rates at which these changes occurred could be measured by placing some of the separated uranium salt and the uranium X in two similar ionization chambers, and by observing the variations in the saturation currents, after covering the substances with aluminium foil to exclude α-rays. It was thus found that the rate of recovery of the activity of the uranium salt was equal to the rate of decay of the uranium X, and that both changes followed the monomolecular law of chemical reactions, by which the rate of change was proportional to the amount of substance present at any instant. Further, if the aluminium screens were omitted in these experiments, the separated uranium salt had an increased activity, whose origin was, therefore, presumably in the emission of α-rays. To summarize, it appeared that uranium could produce uranium X and emit α-rays, while the product could also break up, yielding β-rays, both changes being spontaneous and continuous. It was found that in any change, characteristic α- or β-rays were emitted, but not both together. It has thus become customary to speak of α- or β-ray changes. We may formulate the above changes as follows :—

$$\text{Uranium} \xrightarrow{\alpha} \text{Uranium X} \xrightarrow{\beta}$$

It is unnecessary to explain how the relations of the long chains of radioactive substances have been elucidated. It has been found, for instance, that uranium X is the ultimate parent of ionium, which, in turn, gives rise to radium. This accounts for the presence of radium in uranium-bearing minerals. Radium is the parent of radium emanation, a gas belonging to the group of inert elements, which, in turn, produces radium A, and so on down a long chain, each change being associated with either an α- or β-ray change. The γ-rays appear with β-ray changes. There are two series of radioactive elements, which commence

with the elements uranium and thorium, the final product being the element lead in each case.

Radioactive change is clearly *an atomic phenomenon*. The transmutation of the elements, so long the philosopher's dream, is realized in nature. It is, perhaps, with some sense of disappointment that it is found impossible to control the changes in any way. They are spontaneous and eternal; the atoms break up in a perfectly ordered fashion, independent of imposed conditions so far as is known, each atom yielding a new atom, with the emission of the energy difference between the new state and the old. This is consistent with the conception that the atoms of different elements possess similar structures, and some basis may be seen for the view that atoms differ only in the number and arrangement of the units composing them.

When the rates at which these changes occur are compared for different members of a chain, as measured by the ionization method, it is striking to notice how varied they are, though all obey the monomolecular law. The time of half-decay, that is, the time taken for the given radioactive substance to lose half its activity, may vary from thousands of millions of years (as in the cases of uranium and thorium) to a fraction of a second. For radium itself, this time is about 2000 years, and is *the same for the metal as any of its salts*. This fact conclusively proves that the phenomenon is atomic, depending on the radioactive element alone. This is exactly what the pioneers in this field believed.[13]

19. Radioactive Equilibrium

The results of the previous section have tended to show that the radioactive elements fall in a natural manner into series, in harmony with the disintegration theory of Rutherford and Soddy.[14] The life-history of a single atomic structure might not reveal much about the rate of change as a whole. It is only possible to say that one in a certain number of atoms of a given element decomposes per second. If this number in a given case is y, then y is a constant for the element, which by integration may be shown to be the period of average life in seconds. The fractional amount changing in unit time is known as the radioactive constant of the element, which may be written as $k = 1/y$, and if x is the number of atoms of the element present at any given instant,[15]

$$\frac{dx}{dt} = -kx \qquad . \quad . \quad . \quad . \quad (1)$$

which is the familiar expression for a monomolecular change. This relation may also be written in its integrated form—

$$\frac{x_t}{x_0} = e^{-kt} \quad . \quad . \quad . \quad . \quad (2)$$

where x_0 is the number of atoms present at any time, and x_t the number remaining after time t seconds. If $x_t = \frac{1}{2}x_0$, then t becomes the time of half-change τ, so that, as may be readily verified,

$$\tau = \frac{\log_e 2}{k} = \frac{1}{1 \cdot 443k} \quad . \quad . \quad . \quad (3)$$

Remembering that $ky = 1$, it is seen that the three quantities k, y, and τ are simply related constants.

It is of interest to inquire whether a radioactive change should be classed as chemical in character or not. That the two varieties of change are really quite distinct will be clear when it is recalled that the value of k above is independent of changes of temperature and pressure, so far as is at present known, whereas the corresponding constant in chemical reactions is very susceptible to such changing conditions. Indeed, the emission of rays would appear to set radioactive change in a class by itself, especially since, as will shortly appear, a new atom may possess a lower atomic weight than its parent.

A given radioactive substance A decomposes at a given instant with a speed depending upon the amount of it present, x_A, and upon its radioactive constant k_A, such that the rate of decomposition is measured by $k_A x_A$. As x decreases, k being constant, this rate will steadily diminish, if A is not being reformed at the same time. Suppose that B is being formed from A, and that B, in turn, produces a third element C. Then, at any instant, there would be equilibrium, if B was formed from A at the same rate as it decomposed to form C. The rate at which B is being produced from A is, however, diminishing, so that the rate at which it forms C will decrease to the same extent, and therefore B, like A, will be diminishing in amount. In the particular case where the value of k for A is very small, it may be supposed that, within the duration of observations, A does not diminish to any appreciable extent; if this holds, the rate of production of B will be constant, and its amount will remain fixed,

It is not difficult to understand that the amounts of A and B are then inversely proportional to their radioactive constants. For, when equilibrium is established, the rates of decomposition of A and B are equal, so we may write $k_A x_A = k_B x_B$, whence $x_A/x_B = k_B/k_A$. Now, the values of k for the parent elements uranium and thorium are so small that their amounts may be regarded as remaining constant, and thus, in the two series, each member breaks up at the same fixed rate, and the quantity of any one element at any instant is constant. A convenient analogy is supplied by the rate of delivery of water from a tank. The height of water in a tank corresponds to x above, and the size of the aperture through which the water passes is analogous to k. If there are several tanks delivering into each other, and the level in the top tank is maintained constant, then the level in any tank will also be constant when equilibrium is established, this level being inversely proportional to the size of the aperture.

To summarize: it has been observed that if the speed of decomposition of a parent element is so slow that its amount may be regarded as remaining constant, then there will be at any instant a fixed amount of each member present, inversely proportional to its individual radioactive constant. In agreement with this, constancy is observed between the proportions of uranium and radium occurring in minerals. If, however, the amount of the first member of a chain cannot be regarded as *constant, then there will still be a constant ratio between* the amounts of any two members of a chain A and B, though *their absolute amounts will slowly decrease.* It has also been noticed that the speed of disintegration is unaffected by any alteration of conditions, and therefore, although the decompositions follow a monomolecular law, the changes cannot be regarded as chemical in nature. One atom in a series changes into another with evolution of energy originally locked within it. The phenomena of a discharge tube have led to the belief that electrons are constituent parts of atoms of matter, and therefore the way is prepared for these striking conclusions.

A list of radioactive constants, brought up to date to 1923, has been given by Meyer.[18]

20. The Alpha Rays

The radiations emitted by the active elements must now be considered individually. The α-rays are discussed in this section.

These rays are characterised by their deflection in an electric field, and by possessing less penetrating power than either the β- or the γ-radiations. Further, they produce scintillations on a fluorescent screen, which consist of separate flashes of light.[17] Regener assumed the stream of rays to consist of separate moving particles, each one of which produced a separate scintillation on a screen.[18] The α-rays resemble the positive rays of a discharge tube, and, like them, appear to consist of a stream of positively-charged particles. It has been possible to test this by experiment, and also to justify the assumption made by Regener that each scintillation corresponds to a separate single particle.

The rays were proved to be streams of particles by their definite ratio of charge to mass, *independent of the emitting radioactive substance.* When the method of Thomson, already described in some detail, in which electric and magnetic fields were superimposed, was applied, it gave a positive result.[19] The ratio of charge to mass was found to be in all cases constant, and equal to half the value of the ratio for the hydrogen ion in electrolysis within limits of experimental error. This ratio for α-rays has been given as 4823 E.M. units per gram, while that of the hydrogen ion is 9647 in the same units. The velocity of emission of the α-particle, measured by the above method, is very high, of the order of $1{\cdot}5 \times 10^9$ cms. per second, or about one-twentieth of the velocity of light. It is also found to be constant for a given element in the series. It is important to notice that the above evidence clearly shows that α-rays are identical, no matter from what radioactive element they are emitted.

With regard to Regener's second assumption, it has been possible to indicate its truth, and at the same time to find the amount of charge carried by the α-ray. Regener succeeded in measuring the total charge carried by a known number of particles, and so deduced the charge borne by a single one. The total charge was measured by allowing the rays to enter a Faraday cylinder (which consists of a carefully insulated metal box with a small aperture to receive the rays) containing an electrode connected to an electrometer. The number of particles bearing this charge was counted from the number of scintillations produced per second per unit area of a fluorescent screen. From this type of experiment, a value of the charge borne by one particle has been obtained as equal to $9{\cdot}58 \times 10^{-10}$ E.S. units.[20] This value is almost exactly twice the value of the electronic charge found by Millikan, i.e.

$4 \cdot 774 \times 10^{-10}$ in the same units. This can scarcely be a coincidence; it seems, therefore, that Regener was justified in his assumption that each particle produced a separate scintillation. It then follows that the α-particle carries two unit charges. The direction of deflection of the rays by an electric field indicates that their charge is positive, hence the α-particle possesses two positive charges, which corresponds to the loss of two negative electrons.

The mass of the α-particle must now be considered. Its charge to mass ratio is one-half of that of the hydrogen ion. The latter carries a single positive charge, and the charge of the α-particle is twice as much. A short consideration will show that the mass of the α-particle is four times as great as that of the hydrogen ion. For, let E_α, E_H be the charges, and M_α, M_H the masses of the α-particle and the hydrogen ion respectively, such that—

$$\frac{E_\alpha}{M_\alpha} = \frac{1}{2} \cdot \frac{E_H}{M_H} \text{ and } E_\alpha = 2 \cdot E_H,$$

from which it follows that $M_\alpha = 4 \cdot M_H$. In this way, the particle possesses a mass of atomic dimensions, equal to 4 on the ordinary hydrogen scale. Now helium, first "discovered" in the sun by Lockyer (who attributed certain lines in the solar spectrum to a hitherto-unknown element) has an atomic weight of 4. Does the α-ray, then, consist of an ion of helium? In 1903, Ramsay and Soddy observed that helium was produced from radium emanation.[21] Rutherford further investigated the matter by carefully sealing one tube into another in which an electric discharge could be passed at low pressure.[22] In this way, when radium emanation was passed into the first tube, the characteristic spectrum of helium was found to develop in the other, *the α-particles having passed through the glass into the* discharge tube. The evidence from all directions converges to the view that the α-particle consists of an atom of helium which has lost two negative electrons, thereby becoming a doubly positively charged helium ion.[23]

Now, if an α-ray change occurs by the emission of a single particle from the atom, the element produced should have an atomic weight four units less than its parent. Thus, for example, the determination of the atomic weight of radium emanation by Ramsay and Whytlaw Gray, using a microbalance of special construction, yielded a mean value about 222·4.[24] Taking the

atomic weight of radium as 226·0, there is a loss of 3·6 units of mass by an α-ray change, which agrees fairly well with the above considerations.[25] It therefore appears that an atom of radium breaks up yielding one α-particle and one atom of emanation, and that the helium structure must form part of that of radium and kindred substances.

21. The Scattering of Alpha Rays

The α-rays are of special importance on account of the valuable information supplied by their behaviour in passing through thin metallic sheets and through gases. The path followed by an α-particle in a gas has been photographed by C. T. R. Wilson, using the cloud method mentioned in Chapter II.[26] These results are illustrated diagrammatically in Fig. 17. It is shown that the particles can travel distances of several centimetres in air, but that especially *towards the end of the path* the direction of movement is often abruptly changed. This would be explained if the α-ray were capable of passing *through* atoms of gas, remaining unchanged in direction until it had lost sufficient velocity to be deflected by them. Now the α-particle has atomic mass, so that its passage through matter might be expected to cause disruptive effects, and the results might possibly reveal something about the nature of atomic structures. It is particularly suitable for this purpose, because its velocity of emission from any given radioactive substance is constant. Moreover, the α-particle is conveniently detected by the scintillation of light it produces on a fluorescent screen.

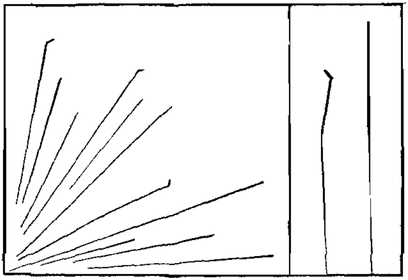
If a narrow band of α-rays is passed through a vacuum on to a sensitive screen, the track is clear and well-defined, as shown by the sharp edges of the spot on the screen. If, now, a thin sheet of gold foil is interposed, these edges become blurred, and the spot is spread out to some extent.[27] This effect is due to "multiple scattering," and is attributed to large numbers of encounters within the foil, occurring in a haphazard manner. It has been shown that the magnitude of the effect can be explained by probability considerations. Scintillations occur, however, in positions which cannot be accounted for by this means. Thus a few particles are turned through large angles, as indicated by Wilson's photographs. This phenomenon is known as "single scattering," and has been studied by Rutherford[28] and Geiger and Marsden.[29] The latter have shown that

the number of particles scattered in a given direction is roughly proportional to the thickness of metallic foil employed. The same workers stated that about one α-particle in 20,000 emitted

FIGURE XVII

PHOTOGRAPHS OF ALPHA-RAY TRACKS
(C. T. R. WILSON)

(*Proc. Roy. Soc.*, 1912; A 87, 292)



The above is a diagrammatic representation of photographs of α-ray tracks from radium obtained by C. T. R. Wilson by the cloud method, the water droplets condensed on the ions produced by the rays being photographed. These photographs provide direct experimental evidence that the constituent parts of atoms occupy but a small fraction of the space enclosed within atomic systems. The α-rays *pass through* the atoms in their path, detaching an electron here and there. So many atoms are ionized that the paths appear continuous in the photographs. The sharp bends occur mainly at the ends of the tracks, where the α-particles have lost most of their velocity, and are attributable to encounters with atomic nuclei. (Somewhat similar tracks have been obtained using β-rays, which, however, show gradual curvature. The tracks of β-rays produced by X-rays are found to be extremely irregular.)

by radium C was turned through 90° in a certain experiment, using a gold foil of thickness 0·0004 mm. It appeared to Rutherford that some kind of rare encounter must be responsible for single scattering of α-rays. Moreover, since the effect increased

proportionally with the thickness of the foil, it seemed probable that some distinct and characteristic part of the atoms of gold was the cause. Here, then, is our first evidence of the Rutherford "nucleus" within an atom.[30] If an atom contains electrons bearing negative charges, and is yet a neutral body as a whole, a positive charge must be connected with it, especially as the negative electrons fail to account for its mass. It will appear later that considerations based on the quantum theory also seem to demand a central nucleus within the atom, responsible for nearly all of its mass. No evidence of anything but negative electrons and positive nuclei in atoms of matter has been obtained. The single scattering of α-particles by matter has been completely accounted for by the theory that an atom contains a single positive nucleus in a central position with attendant negative electrons. The nucleus carries a positive charge equal to that of the whole of these electrons, so that the atom is neutral. This considerable charge on the nucleus and its small size (section 28) has been found to explain the large angles turned through by the α-ray. It will be seen that the repulsion between the positive charges on the α-particle and the nucleus must be very considerable, so that it is only when the former is travelling with very high velocity that it is not turned out of its direct path by a collision.

The nuclear theory of the atom will now be seen to throw light upon the constitution of the α-particle itself. It is clear that this particle must have a very stable configuration, since it is emitted by the disruption of radioactive atoms. Further, it must be related to the helium atom in such a way that it contains two negative electrons less. Now, it is impossible to remove more than two electrons from a neutral helium atom. It therefore seems quite reasonable to suppose that the α-particle is identical with the nucleus of the helium atom, and that this nucleus forms part of the structures of radioactive nuclei, from which it can sometimes be emitted with high velocity. This is a specially important conclusion.

Before leaving this subject, a word should be said with regard to the effect of firing α-particles into the lighter gases. The "range" of an α-particle in hydrogen, or the distance it can travel before its velocity becomes that of the hydrogen molecule at the temperature of the experiment, is about 24 cms. Marsden, however, observed very occasional scintillations up to 82 cms.[31] Rutherford has obtained similar results in air, and has shown the effect to be due to nitrogen, as oxygen does

not manifest it.[32] Now, it may be supposed that in these cases of *lighter atoms, the nuclei may be moved or even broken up* to some extent by the impact of an α-particle. The long range particles in hydrogen and nitrogen have been shown by the usual methods to possess a ratio of charge to mass which proves them to consist of singly positively charged hydrogen. Now, since *doubly positively charged hydrogen atoms have never been observed* in the mass spectrum of hydrogen,[33] or, indeed, anywhere else, it seems inevitable to suppose that the hydrogen atom can part with, and therefore contains one negative electron only, as well as a nucleus bearing a single positive charge. If this is the case, Marsden's observation finds explanation in the suggestion that the impact of α-rays causes certain hydrogen nuclei to be dislodged, and propelled, mostly in a forward direction. As nitrogen can give a similar result, the hydrogen nucleus may enter into the composition of the nucleus of the nitrogen atom. Other light elements which have been found to give hydrogen in a similar way are: boron, fluorine, sodium, aluminium and phosphorus. The effect has not been observed when the atomic weight of an element is a multiple of four, as in the cases of oxygen and carbon. The significance of these results will appear more fully at a later stage (p. 159 *seq.*). It may be mentioned that the cloud method has been utilized by Blackett, who, by photographing simultaneously in two directions at right angles, has overcome the plane projective effect.[34] By this means, the angle between the paths of two nuclei after collision has been calculated. This angle, for the collision between an α-particle and the helium atom, was found to be 89° 45′, in remarkable agreement with the fact that on theoretical grounds, remembering that the masses of the colliding particles are equal, *it should be a right angle. Thus the ordinary* laws of mechanics appear to hold for such impacts.

The α-ray method of probing atomic structure has been treated here in a purely qualitative manner, further detail being reserved to the following chapter.

22. The Beta and Delta Rays

The Curies showed that certain of the rays of radium carried a negative charge.[35] These have properties which make them quite distinct from α-radiation. They are chiefly distinguished from it by their greater penetrating power, by suffering larger deflections under a magnetic field and by emission from a

radioactive substance with much greater velocities, which vary for the same substance. The velocity of β-rays and their ratio of charge to mass has been studied by Kaufmann, using electric and magnetic fields in parallel directions.[86] The rays were thus urged to move in two directions at right angles, as in Thomson's method for positive rays. The curve obtained was not a parahola, though it was continuous. (A short examination of equation (6) on page 54 will show that a parabola should be obtained if the e/m ratio is constant.) It therefore appeared that this ratio varied with the velocity of the rays in a perfectly continuous manner. The results could only be interpreted as showing that the β-ray stream consisted of particles similar to those found in cathode rays, but possessing greater velocities which involved changes in the e/m ratio. Now, according to the theory of relativity, the mass of a particle would increase with its velocity, and it was therefore reasonable to suppose that at velocities approaching that of light the effect had become experimentally discernible. The correction for this variation of mass given by Lorentz was found to be applicable to this case by Bucherer.[87] This supported the view that the mass of the β-ray particle was wholly electromagnetic in origin, since this was assumed in making the calculation. Further, the value of the e/m ratio for slowly-moving particles was found to be identical with that of the electron. Hence no doubt could remain that the β-particle was not only analogous to, but identical with, the cathode ray particle (which was known to be a negative electron). In this way, it was shown that the mass of a negative electron could be regarded as wholly electromagnetic.

The above work supplies further evidence that atoms of matter contain electrons, since the latter are emitted from radioactive atoms. Some difference of opinion exists as to the origin of these electrons. It was at first supposed that they were emitted entirely by the nuclei of radioactive atoms. This theory does not appear to explain their observed variations in velocity. The " spectrum " of velocities exhibits lines as well as a continuous part. Meitner holds that the initial velocity of each β-particle from a given radioactive substance is constant, and that variation is observed because some rays lose energy more than others in overcoming the attraction of the nucleus, and in other ways.[88] The views of Ellis differ from those of Meitner very considerably [89] (section 42).

C. T. R. Wilson has photographed the tracks of β-rays,

using the cloud method.[40] When the photograph is magnified, the results indicate that a very minute number of atoms are onized, and when ionization occurs a single negative electron s detached. Comparison with the photographs obtained using X-rays show that β-rays eject electrons from atoms with much smaller speeds than the former rays. The fact that α- and β-rays can pass through atoms without ionizing them shows hat the electronic constituents of atoms occupy but a small raction of the space enclosed within the atomic system. In one photograph, it was computed that the β-particle had shot hrough as many as 10,000 atoms before it passed near enough o an electron to detach it from the system.

It will be clear that since the emission of a β-ray corresponds o the loss of a negative electron, whose mass is inappreciable compared with that of the atom, the new atom will possess the ame atomic weight. Elements distinct in properties, having he same atomic weight, are known as "isobares."

The scattering of β-rays by matter has also been subjected o experiment.[28, 41]

The δ-rays are emitted by certain radioactive elements, nd are found to be electrons moving with velocities considerbly less than those of cathode rays.[42] They are also produced y the impact of α-rays upon matter.

23. The Gamma Rays

The γ-rays are distinguished from the radiations already escribed by their greater penetrating power and by not being eflected by a magnetic field. In general character, they esemble the X-rays of a discharge tube, and also consist of lectromagnetic waves. This is proved conclusively by the etermination of their wave-length by using reflection from a rystal, and has been accomplished by Rutherford and Andrade, y causing the rays to impinge on a crystal of rock salt at a lancing angle of 1° or less.[43] In this manner, assuming the istance separating the planes of atoms in rock salt, their wavength is found to be less than those of X-rays, and of the order f 10^{-9} cm. The wave-length spectrum of γ-rays exhibits lines, o that several discontinuous wave-lengths are emitted by a iven element. Since X-rays are secondary disturbances in the ischarge tube, produced by the sudden stoppage of a cathode y particle, it would be natural to assume that they are prouced by the sudden stoppage of β-rays within the mass of

radioactive substance, since the two particles are identica. The association of γ-radiations with β-rays, which seems invari able, supports this view. It has also been mentioned that whe γ-rays fall upon a metal, electrons are emitted ("secondary β-rays). The velocity of such electrons has been found t depend upon the frequency of the incident radiation. Thus th action is reciprocal; electromagnetic radiations of short wave length are both produced by electron impact and also ejec electrons. It has been shown by Rutherford that if the genera radiation from radium B and C is allowed to fall upon a gol surface, electrons are emitted whose velocities vary discon tinuously.[44] This, therefore, corresponds to a line spectrum o γ-rays. Evidence has been advanced that some of the mor penetrating waves arise in the nucleus of the radioactive atom The work of Ellis on this subject will be considered in Chapte VII.

In concluding this brief study of the rays emitted by radio active substances, it is noteworthy that similarity in natur exists between—

1. Alpha rays and positive rays,
2. Beta rays and cathode rays,
3. Gamma rays and X-rays.

The following chapter contains a study of the radioactiv isotopes and isobares and of the relation of the radioactiv series to the periodic classification of the elements.

For literature relating to the rise and development of radic activity up to 1904, a list drawn up by Iklé may be consulted.[4]

REFERENCES: (IV)

See Nos. 1, 3, *and* 6 *in the Bibliographical List at end of book*

1 (p. 81) H. Becquerel: "Sur les radiations émises par phosphorescence" *Compt. Rend.*, 1896; **122**, 420, 501. See also *ibid.*, pp. 559 689, 762, 1086.

2 (p. 81) S. P. Thompson: "On Hyperphosphorescence"; *Phil. Mag* 1896; (v.) **42**, 103.

3 (p. 81) P. Curie and (Mme.) Curie: "Sur une substance nouvelle radio active, contenue dans la pechblende"; *Compt. Rend.*, 1898 **127**, 175, 1215.

4 (p. 81) E. Demarçay: "Sur le spectre d'une substance radioactive" *Compt. Rend.*, 1898; **127**, 1218: 1899; **129**, 716.

5 (p. 81) E. Rutherford: "Uranium Radiation and the Electrical Con duction produced by it"; *Phil. Mag.*, 1899; (v.) **47**, 109.
R. J. Strutt: "On the Conductivity of Gases under the Bec querel Rays"; *Phil. Trans.*, 1901; **A196**, 507.

6 (p. 81) P. Curie and (Mme.) Curie: "Effets chimiques produits par les rayons de Becquerel"; *Compt. Rend.*, 1899; **129**, 823.
7 (p. 81) (Mme.) S. Curie: "Sur le poids atomique de radium"; *Compt. Rend.*, 1902; **135**, 161.
8 (p. 82) E. Dorn: "Sur les rayons du radium"; *Compt. Rend.*, 1900; **130**, 1126.
9 (p. 82) F. Giesel: "Ueber die Ablenkbarkeit der Becquerelstrahlen im magnetischen Felde"; *Wied. Ann.*, 1899; **69**, 834.
H. Becquerel: "Influence d'un champ electromagnétique sur le rayonnement des corps radioactifs"; *Compt. Rend.*, 1899; **129**, 996.
10 (p. 82) P. Curie: "Action d'un champ magnétique sur les rayons de Becquerel. Rayons déviés et non déviés"; *Compt. Rend.*, 1900; **130**, 73, 77.
11 (p. 82) E. Rutherford: "Radioactivity produced in Substances by the Action of Thorium Compounds"; *Phil. Mag.*, 1900; (v.) **49**, 161. See also papers quoted at references Nos. 5 and 14.
12 (p. 83) W. Crookes: "Radioactivity of Uranium"; *Proc. Roy. Soc.*, 1900; **66**, 409.
13 (p. 85) H. Becquerel: "Sur la radioactivité de l'uranium"; *Compt. Rend.*, 1901; **133**, 977.
P. Curie and (Mme.) Curie: "Sur les corps radioactifs"; *Compt. Rend.*, 1902; **134**, 85.
14 (p. 85) E. Rutherford and F. Soddy: "The Cause and Nature of Radioactivity"; *Phil. Mag.*, 1902; (vi.) **4**, 370, 569: 1903; (vi.) **5**, 576.
E. Rutherford: "The Succession of Changes in Radioactive Bodies"; *Phil. Trans*, 1905; **A204**, 169.
15 (p. 85) *Idem*: A Radioactive Substance emitted from Thorium Compounds"; *Phil. Mag.*, 1900; (v.) **49**, 1.
16 (p. 87) S. Meyer: "Radioaktiven Kostanten nach dem Stand von 1923"; *Jahr. Rad. Elekt.*, 1923; **19**, 334. See also *Chem. and Ind.*, 1923; **42**, 175.
17 (p. 88) W. Crookes: "The Emanation of Radium"; *Proc. Roy. Soc.*, 1903; **71**, 405.
18 (p. 88) E. Regener: "Die Zahlung der α-Teilchen durch die Szintillation und die Grösse des elektrischen Elementarquantums"; *Verh. Deut. Phys. Ges.*, 1908; **10**, 78: *Berl. Ber.*, 1909; **28**, 948.
E. Rutherford and H. Geiger: "An Electrical Method of Counting the Number of α-Particles from Radioactive Substances"; *Proc. Roy. Soc.*, 1908; **A81**, 141.
19 (p. 88) E. Rutherford: "The Mass and Velocity of the α-Particles expelled from Radium and Actinium"; *Phil. Mag.*, 1906; (vi.) **12**, 348.
Idem: "The Velocity and Energy of the α-Particles from Radioactive Substances"; *Phil. Mag.*, 1906; (vi.) **13**, 110.
20 (p. 88) E. Rutherford and H. Geiger: "The Charge and Nature of the α-Particle"; *Proc. Roy. Soc.*, 1908; **A81**, 162.
21 (p. 89) W. Ramsay and F. Soddy: "Experiments in Radioactivity, and the Production of Helium from Radium"; *Proc. Roy. Soc.*, 1904; **72**, 204: **73**, 346.
22 (p. 89) E. Rutherford and T. Royds: "The Nature of the α-Particle from Radioactive Substances"; *Phil. Mag.*, 1909; (vi.) **17**, 281.

23 (p. 89) B. B. BOLTWOOD and E. RUTHERFORD: "Production of Helium from Radium"; *Phil. Mag.*, 1911; (vi.) **22**, 586.
24 (p. 89) R. WHYTLAW GRAY and W. RAMSAY: "The Density of Niton (Radium Emanation) and the Disintegration Theory"; *Proc. Roy. Soc.*, 1910; **A84**, 536.
25 (p. 90) *Idem*: "The Atomic Weight of Radium"; *Proc. Roy. Soc.*, 1911; **A86**, 270.
26 (p. 90) C. T. R. WILSON: "On a Method of Making Visible the Paths of Ionising Particles through a Gas"; *Proc. Roy. Soc.*, 1911; **A85**, 285.
Idem: "Expansion Apparatus for making Visible the Tracks of Ionising Particles in Gases, and the Results obtained by its Use"; *Proc. Roy. Soc.*, 1912; **A87**, 277.
27 (p. 90) H. GEIGER: "Scattering of α-Particles by Matter"; *Proc. Roy. Soc.*, 1910; **A83**, 492.
28 (p. 90) E. RUTHERFORD: "The Scattering of α- and β-Particles by Matter, and the Structure of the Atom"; *Phil. Mag.*, 1911; (vi.) **21**, 669.
29 (p. 90) H. GEIGER and E. MARSDEN: "The Laws of Deflexion of α-Particles through Large Angles"; *Phil. Mag.*, 1913; (vi.) **25**, 604.
30 (p. 92) E. RUTHERFORD: "The Structure of the Atom"; *Phil. Mag.*, 1914; (vi.) **27**, 488.
Idem: "Nuclear Constitution of Atoms"; *Proc. Roy. Soc.*, 1920; **A97**, 374.
31 (p. 92) E. MARSDEN: "The Passage of α-Particles through Hydrogen"; *Phil. Mag.*, 1914; (vi.) **27**, 824.
E. MARSDEN and W. C. LANTSBERRY: *Phil. Mag.*, 1915; (vi.) **30**, 240.
32 (p. 93) E. RUTHERFORD: "Collision of α-Particles with Light Atoms"; *Phil. Mag.*, 1919; (vi.) **37**, 537. See also Ref No. 30 above.
33 (p. 93) J. J. THOMSON: "Multiply Charged Atoms"; *Phil. Mag.*, 1912; (vi.) **24**, 668.
34 (p. 93) P. M. S. BLACKETT: "Analysis of α-Ray Photographs"; *Proc. Roy. Soc.*, 1922; **A102**, 294.
Idem: "Study of Forked α-Ray Tracks"; *Proc. Roy. Soc.*, 1923; **A103**, 62.
W. D. HARKINS and R. W. RYAN: "A Method for Photographing the Disintegration of an Atom, and a New Type of Rays"; *J. Amer. Chem. Soc.*, 1923; **45**, 2095.
35 (p. 93) P. CURIE and (Mme.) CURIE: "Sur la charge électrique des rayons déviables du radium"; *Compt. Rend.*, 1900; **130**, 647.
36 (p. 94) W. KAUFMANN: "Methode zur Bestimmung von Ladung und Geschwindigkeit der Becquerelstrahlen"; *Phys. Z.*, 1900; **2**, 602.
Idem: "Die electromagnetische Mass des Elektrons"; *Phys. Z.*, 1902; **4**, 54.
37 (p. 94) A. H. BUCHERER: "Die experimentelle Bestatigung des Relativitätsprinzips"; *Phys. Z.*, 1908; **9**, 755: *Ann. Physik*, 1909; (iv.) **28**, 513.
W. KAUFMANN: "La déviation magnétique et électrique des rayons Becquerel et la masse électromagnétique des electrons"; *Compt. Rend.*, 1902; **135**, 577.
38 (p. 94) L. MEITNER: "Über die Entstehung der β-Strahl Spektren radioaktiver Substanzen"; *Z. Physik*, 1922; **9**, 131.

38 (p. 94) *Idem*: "Über der Zusammenhang zwischen β- und γ-Strahlen"; *Z. Physik*, 1922; **9**, 145: **11**, 35.
39 (p. 94) C. D. ELLIS: "Interpretation of β-Ray and γ-Ray Spectra"; *Proc. Camb. Phil. Soc.*, 1922; **21**, 121.
Idem: "The β-Rays of Uranium X_1"; *Nature*, 1924; **113**, 290.
40 (p. 95) C. T. R. WILSON: "Investigations on X-Rays and β-Rays by the Cloud Method"; *Proc. Roy. Soc.*, 1923; **A104**, 1, 192.
41 (p. 95) H. GEIGER and W. BOTHE: "Über Zerstreuung im β-Strahlen in dünnen Metallfolien"; *Phys. Z.*, 1921; **22**, 585.
J. A. CROWTHER and B. J. F. SCHONLAND: "On the Scattering of β-Rays"; *Proc. Roy. Soc.*, 1922; **A100**, 526.
42 (p. 95) J. J. THOMSON: "On the Positive Electrification of α-Rays, and the Emission of Slowly Moving Catohde Rays by Radioactive Substances"; *Proc. Camb. Phil. Soc.*, 1904; **13**, 49.
43 (p. 95) E. RUTHERFORD and E. N. DA C. ANDRADE: "The Wave-Lengths of the Soft γ-Rays from Radium B"; *Phil. Mag.*, 1914; (vi.) **27**, 854.
44 (p. 96) E. RUTHERFORD, H. ROBINSON, and W. F. RAWLINSON: "Spectrum of the β-Rays excited by the γ-Rays"; *Phil. Mag.*, 1914; (vi.) **28**, 281.
45 (p. 96) M. IKLÉ: "Literatur der Radioaktivität vor dem Jahre 1904"; *Jahr. Rad. Elekt.*, 1905; **1**, 413.

CHAPTER V

THE ELECTRONIC CONSTITUTION OF ATOMS

24. The Emission of Electrons from Matter

THE lines of evidence so far considered in support of the view that electrons are present in atomic structures may now be reviewed. This evidence falls naturally into three groups. In the first place, the variations in speeds of negatively-charged gaseous ions with reduction in pressure lead to this conclusion. Further, electrons appear as cathode rays in the discharge tube at low pressures, having arisen from residual gas molecules by ionization. Secondly, radioactive atoms are a source of electrons, emitted spontaneously and with very high velocity. Lastly, electrons are liberated when certain radiations fall upon matter, for example, when γ-rays fall upon a metallic surface. Certain somewhat simpler experiments show the same result. Electrons may be evolved from a metal by the action of ultraviolet light (the "photoelectric" effect of Hertz), and they may be produced when the metal becomes heated.[1] These last methods fall into one group, as heat waves and X-rays are both, like light, electromagnetic waves. Evidence for this will be given in the next chapter. It is here specially worthy of note that various independent methods exist of causing matter to emit *the same fundamental entity*, the electron. The ratio of charge to mass gives practically constant values in all cases, being independent of velocity, except for the relativity correction at high speeds already mentioned. Thus it may be stated quite definitely that the negative electron forms part of the structure of all atoms.

The experiments on the single scattering of α-rays have led to the belief that, beside electrons, an atom contains a single nucleus, bearing a positive charge equal to that carried by all the extranuclear electrons. All atoms are built up of the same fundamental building units, and must differ only in their number

and arrangement. No evidence has been found leading to the conclusion that there is anything in the composition of an atom other than these electrons and the central nucleus, so that it would appear to resemble a tiny solar system, though the analogy is incomplete. The nucleus itself will be shown to be complex in all cases but that of hydrogen, and to contain both positive and negative electrons. Further, the penetration of matter by various rays considered show that the atom is really a highly disperse structure, containing spaces and distances which are large compared with the sizes of the building units. In fact, the density of an atom appears to be zero everywhere, except at a very few isolated points where an electron or a nucleus happen to be. At these points, the density may be very great indeed, possibly many thousand times as much as that of the material in bulk. The main point is that the units of which such an atom is built are decided upon, and the sequel will be mainly concerned with the numbers, arrangements, and possible movements of these units in different atoms.

It should be pointed out that the widely varying velocities with which electrons are emitted and other facts, such as the existence of isotopes, indicate that they may be held by atoms with different degrees of firmness. Indeed, it must not rashly be concluded that in all cases the electrons are constituent parts of atoms. It is generally admitted that there are several types of electrons in matter, which vary only in the magnitude of the forces which bind them to it. First, there may be free electrons in matter. The movements of these may be held responsible for thermal conduction, in a way analogous to the behaviour of gas molecules according to kinetic theory. In the second place, electrons may be weakly bound to atoms. Such electrons are split off when an atom becomes an ion. Thirdly, to account for the individual properties of atoms and ions, as, for example, their characteristic X-ray spectra, further electrons still more closely bound are postulated. Lastly, there exists the possibility that both kinds of electrons are present within the nucleus itself. It will be seen that this supposition is necessary to explain the existence of isotopes, and for other reasons. Generally speaking, the electrons which are outside the nucleus have been supposed to be responsible for the spectra of the elements, and for their chemical properties, whereas the nucleus is associated with the radioactive properties of the atom. Physical properties, except those depending on mass, are also connected with the external electrons. The reasonableness of this view

will be clearer as the subject develops. The above division of electrons into classes is only provisional. The present purpose is to emphasize the fact that all electrons are not bound to the atom in the same way.

25. Atomic Numbers

The atomic number of an element is often defined as its ordinal number in the series of elements when they are arranged in order of ascending atomic weights. This definition, however, would appear to be somewhat unsatisfactory, in view of the vacant spaces in the periodic table, and on account of the anomalous cases of argon and potassium, of cobalt and nickel, and of tellurium and iodine. Thus, argon is counted as number 18 and potassium as 19, though the atomic weight of argon is greater than that of potassium. The earliest vacant space occurs after element number 42, which is molybdenum. The next known element in order of ascending atomic weight is ruthenium, which, according to the above definition, would be number 43, whereas it is counted as 44 on account of the vacant space. It is perhaps best, therefore, in attempting to make a definition, to connect atomic number with the ordinal *number of the compartment occupied in the periodic table.* Thus, hydrogen is number 1, helium number 2, and so on. (See Table I, frontispiece.) In this way, the vacant spaces are counted, and because it is necessary to place argon before potassium in the periodic arrangement, these two elements are also numbered in this order. Triads such as iron, cobalt, and nickel must be placed in separate compartments for this purpose. The rare earths fit in quite naturally, and hafnium, which follows them, is number 72. This brings uranium correctly as number 92. The empty spaces have odd numbers: 43, 61, 75, 85 and 87.

The possible significance of atomic numbers was first indicated by van den Broek in 1915.[3] The suggestion was made that the results on the scattering of α-particles by matter were consistent with the view that the charge on the nucleus of an atom could be expressed by this number. Indeed, if atomic nuclei contain electrons, their charges should be always whole multiples of the electronic charge. Further, considerations of the charges carried by ions (section 8) are quite consistent with the conception that one additional negative electron is carried from one element to the next in the periodic arrangement,

with corresponding increase of valency of one unit. The suggestion mentioned above was proved to be a correct one by the pioneer investigation of Moseley and the confirmatory experiments of Chadwick.

26. Secondary X-Rays and Nuclear Charge

It has been observed that X-rays are set in motion when cathode rays fall upon an obstacle in their path. Barkla had conducted experiments upon the "secondary" radiations produced when X-rays fall upon matter. It was found possible to distinguish between two classes of these secondary radiations.[3] The first of these was called "scattered" radiation, and was indistinguishable in general character from the incident rays. Thus, it possessed about the same penetrating power, and if the incident radiation was not homogeneous, then it also showed the same nature. The second type of radiation, termed "characteristic" radiation, consisted of a limited number of wave-lengths, which were dependent only upon the particular atoms encountered by the rays. It was found to be less hard, i.e., less penetrating, than the incident rays. Barkla showed that the characteristic radiation of an atom consisted of at least two wave-lengths, one of which was harder than the other, as shown by their different penetrating power in aluminium. In analysing the rays emitted by the elements from silver to barium in the periodic table, he proved that both classes were present. The harder rays were named "K" rays, and the softer, "L" rays. As a result of his absorption measurements, Barkla stated that the K radiation from cerium was more than a thousand times as penetrating as the L radiation from silver. The K-rays were most easily observable in the lighter elements. Further series, known as M-rays,[4] and N-rays[5] have been investigated for the elements of highest atomic number. These secondary X-rays must be attributed to the atom because they are characteristic of a given element, and *independent of its state of chemical combination.* Thus a compound gives the spectra of its constituent elements. The lines of any one series were found to be related to each other in a definite way. It was further shown by Kaye that the characteristic X-ray spectrum of an atom was emitted when cathode rays fell upon it.

Previous to the work of Moseley, the idea that the number of negative electrons in an atom was equal to about half the

atomic weight of the element had been gradually gaining ground. Two independent lines of evidence had led to this conclusion. In the first place, Rutherford had derived this from his experiments on the scattering of α-rays by matter. It was assumed that the "inverse square" law of repulsion held good for the collision between the α-particle and the nucleus of an atom. In these circumstances, classical mechanics indicated that the path of the former was hyperbolic in shape. It has been shown by Darwin that the experiments of Geiger and Marsden are consistent with the inverse square law assumption.[6] On this basis, Rutherford, in 1911, deduced an expression for the fraction ρ of the total number of particles which were deflected through an angle greater than a given angle ϕ :—

$$\rho = \pi n t \frac{Z^2 e^4}{T^2} \cdot \cot^2 \frac{\phi}{2} \quad . \quad . \quad . \quad (1)$$

where t is the thickness of the interposed sheet of matter, n the number of atoms in unit volume, Z the number of unit charges carried by the nucleus, T the kinetic energy of the moving particle and e the electronic charge. Now ρ could be determined experimentally by the method of counting scintillations on a screen, and from this the value of Z could be derived. Rutherford, using results obtained by Geiger and Marsden with α-rays and of Crowther with β-rays, concluded that the charge borne by the nucleus was proportional to the weight of the atom.[7] He also gave the following relation for the fractional number of particles Y/Q deflected through an angle ϕ falling on unit area of a fluorescent screen :—

$$\frac{Y}{Q} = \frac{ntb^2 \operatorname{cosec}^4 \frac{\phi}{2}}{16r^2} \quad . \quad . \quad . \quad . \quad (2)$$

where Y was the number of particles falling on unit area in unit time deflected through the angle ϕ, Q the total number, r the distance between the point of incidence of the rays on the scattering material and the screen, and b was the nearest distance of approach of the particle to the heavy nucleus such that—

$$b = \frac{2ZeE}{mv^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Ze, E and e were the charges on the heavy nucleus, α-particle and electron respectively, and m, v the mass and velocity of the α-particle. Geiger and Marsden confirmed the

conclusion of Rutherford that the equations above led to values of the nuclear charge equal to about half the weight of scattering atom.[8] Rutherford and Nuttall reached the same conclusion by experiments on the scattering of α-particles by gases.[9]

Barkla made similar deductions as a consequence of his experiments on the scattering of X-rays by atoms.[10] He studied the scattering produced by atoms from phosphorus to sulphur in the periodic table, and found that the scattering was roughly proportional to the mass of the atom when equal numbers of atoms were considered. The intensity of the scattered radiation in the case of a gas varied directly as the density.[11] The varying ability of the elements to scatter X-radiation was attributed by Barkla to the different numbers of electrons in their atoms. Thomson had deduced the following relation between the energy E of the primary radiation per c.cm. and energy E_1 of radiation scattered per c.cm. of the medium :—

$$E_1 = \frac{8}{3}\pi\frac{n_1 e^4}{m^2} . E \quad . \quad . \quad . \quad (4)$$

where n_1 was the number of scattering centres per c.cm.[12] Barkla showed that if the electrons were the scattering centres, their number n_1 was roughly equal to half the weight of the scattering atom.

Before the publication of the work of Moseley, then, it appeared to have been established that the hydrogen atom contained, apart from the nucleus, one (negative) electron only, while other atoms had numbers of electrons (equal to the nuclear charge) which were about half their atomic weights. It may be noticed that the suggestion that the hydrogen atom contained one electron only aroused considerable interest and not a little surprise. In this connection, the following words, written by Lodge in 1906, may be of interest: "This is an extraordinary and unexpected result, and at first sight appears very unlikely, since the ordinary chemical assumption of unit atomic weight for hydrogen has always been known to be a pure convention, made for convenience alone, and not likely to correspond with anything in nature. I do not suppose that anyone imagined that it would, even provisionally, be found to have a physical and rational basis." [13]

The evidence that the hydrogen and helium atoms have respectively one and two extranuclear electrons is given in section 21 (pp. 91, 92). Mosley's work described in the following section, is in harmony with this view.

27. High Frequency Spectra of the Elements

Moseley, in 1913, published an important paper in which the fundamental significance of the conception of atomic number was pointed out.[14] He modified the apparatus used by Kaye to prove that a sufficiently fast stream of cathode rays caused an element to emit its own characteristic X-radiation. In Moseley's experiment, a stream of cathode rays was passed through a fine slit on to the substance under investigation in a highly exhausted discharge tube. The X-rays thus set up were passed through a fine slit and then through a thin aluminium window. They were received on the cleavage plane of a large crystal of potassium ferrocyanide mounted on a spectrometer table. This crystal was used to determine the wave-lengths, and, therefore, the frequencies of the rays, by Bragg's method. The value of the distance between successive layers in the crystal, known as the "grating constant" d, had been obtained by comparing it with a crystal of rock salt whose value of d had been determined once for all. Moseley used a photographic plate to receive the reflected beam. Each characteristic wave-length gave a short curved line on development. The order of spectrum was determined by photographing each spectrum in the second as well as the third order. The arrangement of apparatus is depicted in Fig. 18.

The characteristic X-ray spectra of different elements were photographed by Moseley by changing the anticathode used. The glancing angle θ, producing a given line, was deduced from the position of the line on the plate and the dimensions of the apparatus, and thus the corresponding wave-length λ could be calculated from the relation $n\lambda = 2d \cdot \sin \theta$. The frequency of the line was then calculated from the velocity of light, by dividing this quantity by the wave-length found. It was discovered that in the spectra of different elements there were lines which, though of different frequency, corresponded to each other in relative position and also roughly in intensity. Moseley found two lines in the K series in each case, of which one was more marked than the other. There were also several lines of the L series. Considering, now, the stronger K line for a series of elements, he was able to show that a certain quantity Q, which was proportional to the square root of the frequency of the line for a given element, differed by unity in passing from one element to the next element in the periodic system. Thus, it was possible to write an equation as follows :—

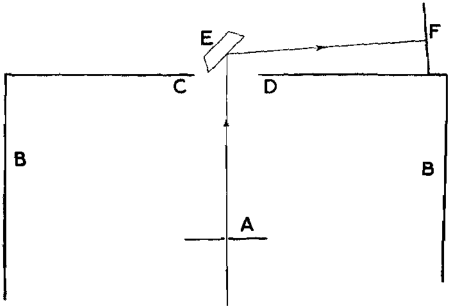
$$\nu = a(Z - 1)^2 = aQ_K^2 \quad . \quad . \quad . \quad (5)$$

where a was a constant for the particular line considered, and ν the frequency of the line for an element of atomic number Z. Thus the values of Q_K for iron, cobalt and nickel were found to be 24·99, 26·00 and 27·04 respectively, the atomic numbers of these elements being 26, 27 and 28. *Hence, the square root of*

Figure XVIII

APPARATUS FOR HIGH FREQUENCY SPECTRA (MOSELEY)

(*Phil. Mag.*, 1913; (vi) **26**, 1025)



A. *Slit through which X-ray beam passes.*
B. Leaden box to screen the rays.
C D. Aluminium window, 0·02 mm. thick.
E. Crystal of potassium ferrocyanide, mounted on the prism table of a spectrometer.
F. Photographic plate, mounted on spectrometer arm.

the frequency gave a linear relationship with the atomic number. The constant a was different for the other K line, equation (5) remaining otherwise the same. With the L series, $Q_L = (Z - 7{\cdot}4)$, so that a more general expression was the following :—

$$\nu = a(Z - b)^2 \quad . \quad . \quad . \quad . \quad (6)$$

where b was constant for a given series, and a varied from line to line of the series, being constant only for a given line, both a and b being independent of Z.

Several important conclusions followed at once from the above work. The accuracy with which the above relation was found to hold for the earlier elements showed that if Z was 42 for molybdenum, it must be 44 for ruthenium, and this fitted in perfectly well with the periodic classification, which demanded a missing element between these two. The same result was found where other elements were missing in the periodic table. Further, the values of Q for iron, cobalt, and nickel given above showed that, in agreement with the chemical properties of these elements, cobalt was to be placed before nickel, in spite of its greater atomic weight, and similarly argon came before potassium, and tellurium before iodine. The X-ray method has also proved of value in establishing the individuality of the rare earths as elements, which result had been previously reached only after extremely tedious processes of fractional crystallization. It has also led to the proof of the existence of hafnium (celtium), which fitted in an empty space in the periodic table at atomic number 72.[15]

It is noteworthy that the X-ray spectra of the elements are much simpler in character than their optical spectra. It has, therefore, been supposed that the X-ray spectra originate in the movements of electrons in the inner system of an atom, which presumably does not change very considerably in passing from one element to the next. The optical spectra, on the other hand, have been assigned to movements in the outer sphere of the atom. It is not possible to follow this matter more fully here, and it will be further treated in section 44. Now, if this theory of the origin of X-ray spectra is for the moment accepted, then it would appear that the K series, being the most penetrating, originates nearest to the nucleus itself, the L series coming from electron movements further away from the nucleus, and so on. This suggests the presence of " rings " of outer electrons, which may be assumed for the present (see p. 169). Now an electron in the innermost ring (in which the K-rays presumably originate) experiences practically the whole positive charge of the nucleus, so that if Z in equation (6) represents the charge on the nucleus, its effect would be expected to be reduced by only a small amount, due to the repulsion of other electrons charged with the same sign (i.e. negative) in the ring. This finds expression in the fact that the constant b is smallest for

the K-rays. For the L series, *b* rises to 7·4, indicating that a negative electron in the L ring experiences a smaller attraction to the centre due to the "shielding effect" of negative electrons of the K ring which are between it and the nucleus, as well as the repulsive effect of electrons in its own ring. If this is granted, then it is clear that *Z* will correspond to the charge on the nucleus. It will also give the number of extranuclear negative electrons in an atom which balance this positive charge. Moseley referred to the conclusions of Rutherford and Barkla already cited, and concluded that the atomic number of an atom actually had this significance.

The experiments of Chadwick have supplied confirmatory evidence.[16] Applying equation (2) on page 104 to the number of particles scattered through a given solid angle, obtained by the use of an ingeniously contrived apparatus, he was able to derive values of the nuclear charge of three elements which agreed with their atomic numbers within 1 per cent. For copper, silver and platinum, the values obtained were 29·3, 46·3 and 77·4 respectively, their atomic numbers being 29, 47 and 78. This is direct evidence in favour of the view that the atomic number of an atom measures the charge borne by the nucleus.

The heaviest atom at present known is that of uranium, which has an atomic number of 92. In this instance, the nucleus carries a charge $92e$ where e is the electronic charge, and there are 92 electrons external to the nucleus. This number of electrons, however, would in no way account for the atomic weight of 238, so that it follows, as already noticed, that the masses of all atoms are dependent on their nuclei. Further, since the hydrogen nucleus or proton has unit mass, the uranium nucleus must contain 238 protons. Since this leads to a charge of 238 positive units, the nucleus also contains $238 - 92 = 146$ negative electrons. The uranium nucleus, therefore, appears to contain no less than $238 + 146 = 384$ electrons of both kinds. This serves to show the extreme complexity of the nucleus of a heavy atom. That this large number of electrons is packed in a very small space will appear, from considerations advanced, in the following section.

28. The Size of the Nucleus

Equation (3) on page 104 has enabled estimates of the sizes of atomic nuclei to be made. In the case of the α-particle,

$E = 2e$, so that we have—

$$b = \frac{4Ze^2}{mv^2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where m is equal to four times the mass of a hydrogen atom. The velocity of the α-particle is known, and depends on the radioactive substance from which it is emitted. Further, Z and e are known, so that it is possible to determine b, the nearest distance of approach of an α-particle to a heavy nucleus bearing charge Ze. By evaluating these constants for a gold atom, a value of $b = 3 \times 10^{-12}$ cm. is obtained. The radius of a gold nucleus must be less than this amount. In cases where the struck nucleus cannot be regarded as stationary, the matter is rather more complicated. It is, nevertheless, amenable to treatment by mechanical considerations. Values of b for the α-particle in collision with hydrogen nuclei lead to the conclusion that this particle is contained within a boundary of oblate spheroidal form, having semi-axes 4×10^{-13} and 8×10^{-13} cm. Within these distances, the inverse square law appears to break down, so that they may be regarded as giving the shape and size of the helium nucleus. From the photographic study of forked tracks already mentioned, Blackett has shown that the inverse square law holds when the distance between the argon nucleus and the α-particle lies between 7×10^{-12} and 10^{-9} cm. It appears that, below the former limit, the law no longer holds on account of the intense field of the nucleus, and that the nuclei of atoms have diameters of the order of 10^{-12} cm. It is somewhat difficult to define what is meant by the diameter of an atomic nucleus, but the above result represents the boundaries within which the inverse square law breaks down.

In section 11, by considerations based on Thomson's relation connecting the electromagnetic mass of a small charged particle with its radius (equation (9) on p. 38), the radius of a positive electron was found to be considerably less than that of the negative electron. These considerations lead to a radius of the positive electron (i.e., the hydrogen nucleus) of about 10^{-16} cm. At the other extreme in the periodic system, it has been calculated that the diameter of a platinum nucleus is of the order of 10^{-12} cm. In general, the sizes of atomic nuclei are approximately the sums of the sizes of their constituent particles.

In every atom, therefore, there is one minute nucleus which bears nearly all the mass of the atom, and, in addition, a definite number of electrons of the negative variety equal to th

atomic number of the element. The existence of definite series of characteristic X-rays of each atom points to some regular arrangement of these outer electrons. The importance of the conception of atomic number will now be evident. Moseley emphasized it as more fundamental than that of atomic weight.

29. Isotopes and Isobares

Some leading features of the historical aspect of the subject of isotopes will now be considered. In 1902, it was found, with some surprise, that radium and thorium emanations condensed at practically the same temperature.[17] Boltwood, in 1906, discovered a new element in the radioactive group, for which he proposed the name " ionium," and found it to possess chemical properties closely resembling those of thorium.[18] It was observed by Marckwald and Keetman that a chemical separation of a mixture of the compounds of ionium and thorium could not be effected.[19] For instance, thorium and ionium carbonates were both soluble in ammonium carbonate solution, and behaved in other ways as if chemically identical, though the atomic weights of the two elements were known to be different. Further, these two elements had different speeds of radioactive change, so that their remarkable chemical similarity began to arouse interest. Their inseparability by chemical means was confirmed by von Welsbach.[20] In 1907, Hahn discovered mesothorium I.[21] A little later, Marckwald failed to produce any separation between salts of mesothorium I and those of radium by chemical means, using the most delicate apparatus available.[22] The conclusion was reached that the feat was impossible. Other cases were soon forthcoming. The work of Elster and Geitel, and others, showed that radiothorium was also inseparable from thorium.[23] Further, when an attempt was made to fit these elements into the periodic table, it appeared that the elements which were indistinguishable chemically must occupy the same spaces. By 1910, the idea was gaining ground that two or more elements might exist which were chemically identical, and fitted into the same compartment of the periodic table, but which differed in atomic weight and in radioactive properties. Soddy strongly supported these views, and suggested the name " isotope " (*Gk.* same place) for use in this connection.[24] In 1914, Soddy and Hyman found that the lead from Ceylon thorite possessed a density about

0·26 per cent. higher than ordinary lead, and a chemical determination of atomic weight of lead in Ceylon thorite yielded the value 207·694, whereas ordinary lead had an atomic weight of 207·2.[25] In 1916, Richards and Wadsworth found a value of 206·08 for a sample of lead from the uranium mineral cleveite.[26] Now, these results were in striking agreement with the theory of radioactive changes. Between the element thorium of atomic weight 232 and the end product thorium lead, there were 6 α-ray changes. Since each of these changes involved, according to the theory, a loss of 4 units of atomic weight, the number given by $232 - (6 \times 4) = 208$ should represent the atomic weight of the end product. Similarly, in the uranium series, starting from uranium of atomic weight 238, there were 8 α-ray changes in the formation of uranium lead, the end product, whose atomic weight should be $238 - (8 \times 4) = 206$. Thus the predictions of theory were very well satisfied.

Turning next to the question of the spectra of isotopes, Russell and Rossi, in 1912, observed that a mixture of thorium and ionium oxides appeared to give the same " arc spectrum " as pure thorium oxide.[27] Two years later, Rutherford and Andrade examined the γ-ray spectra of radium B and radium C, the β-rays being removed by a magnetic field.[28] The wave-lengths were measured by the reflection method, using a crystal of sodium chloride. By this means, certain of the softer rays were found to coincide in wave-length within experimental error with lines of the L series of the characteristic X-ray spectra of lead and bismuth respectively. But radium B was considered, according to the theory of radioactivity, to be an isotope of lead, and radium C of bismuth, so that this work indicated that isotopes had the same X-ray spectra. This has been confirmed by Siegbahn and Stenström.[29] Rutherford and Andrade considered that the softer γ-rays arise, like the L-rays, from the extranuclear system. The most penetrating γ-rays had no counterpart in lead and bismuth, and were, therefore, supposed to originate in the nucleus of the radioactive atom. In regard to arc spectra, however, Harkins and Aronberg found that a very small though definite difference in wave-length existed between a certain line of radium lead and that of the corresponding line of ordinary lead.[30] Merton has confirmed this result for several of the corresponding lines of these two isotopes.[31] The Bohr theory of the atom, which follows the Rutherford model, led to the supposition that a slight difference in wave-length should be found.[32] The experimentally observed

difference for a certain line was about 0·005 Ångstrom units, *which was a hundred times as great as that* predicted by the Bohr theory. A further discovery, of importance in this connection, is that the infra-red spectrum of hydrogen chloride reveals a series of double peaks. The frequency difference between the two maxima is constant, and has been attributed by Loomis and Kratzer to the two different hydrogen chloride molecules, with Cl (35) and Cl (37), the agreement being quantitative.[33]

Aston's first paper relating to mass-spectra was published in 1919. In section 16 it has been seen that arising out of this work he was led to extend the conception of isotopes to the non-radioactive elements, showing that an ordinary element such as chlorine may exist in two or more varieties.[34] The conception of an isotope is the same within and without the radioactive series, but it is interesting to observe that in the two cases the problem was tackled from opposite points of view. In the radioactive group, separate elements were first distinguished, and then shown to be inseparable chemically if they happened to become mixed, whereas among the other elements the mixtures of isotopes found in nature were shown to be composite. It thus happens that radioactive isotopes possess different names, in contrast with ordinary isotopes, though the theory of isotopes makes no distinction between the two cases. Thus many of the 87 known elements are actually *mixtures of isotopes, which must be considered to be different* varieties of these elements. The atomic weights of elements were always supposed to be invariable functions of their atoms, because until the discovery of isotopes no difference had ever been detected in specimens of elements from different sources. All the elements examined were apparently uniform mixtures of isotopes. Thus the development of analytical chemistry, which depended on the conception of constancy of atomic weight of an element, became possible, and for the same reason is still almost unaffected by the new discovery. (The general constant proportions of the isotopes of an element found in nature may be explained in the following way. It is supposed that in the process of cooling which resulted in the formation of the earth, protons and electrons combined to build up atoms. If the probability of a certain arrangement being produced was independent of conditions such as rate of cooling, then different varieties of the same element could have been evolved in constant proportions. This matter, however, belongs rather to the realm of speculation. Ordinary lead of constant atomic

weight may be the result of some such building process, as distinct from lead of radioactive origin, formed from the decomposition of an unstable heavier arrangement.)

The next point for consideration is the possibility of the separation of isotopes by physical methods. Kohlweiler claimed to have separated from ordinary iodine a product having an atomic weight 2 per cent. higher than the normal by fractional diffusion.[85] The work of Brönsted and von Hevesy on the separation of the isotopes of mercury by fractional distillation under reduced pressure is particularly convincing.[86] A difference of 0·1 unit of atomic weight was found between the earliest and latest fractions. The extreme difficulty experienced in separating isotopes indicates that if once they became mixed in constant proportions, it is improbable that any natural process brought to bear upon the mixture would change these proportions. Further, the same fact would appear to show that the methods of quantitative chemical analysis are quite inappreciably affected by the discovery of isotopes, as already stated.

The theory of isotopes has thrown light upon the hitherto anomalous positions of argon and potassium in the periodic table. It has been shown, by the positive ray method, that argon consists mainly of the isotope of atomic weight 40 with a small proportion of the isotope of atomic weight 36, while potassium consists mostly of atoms of weight 39, with a relatively small number of atoms of weight 41. Since the ordinary atomic weight is an average depending on the weights and proportions of the atoms of the isotopes present, it follows that the atomic weight of argon will, in the circumstances, be greater than that of potassium. This is a discovery of special interest, and it is possible that similar explanations of other like anomalies in the periodic table will be found.

The existence of isobares has already been mentioned. Such elements possess the same atomic weight but fall into different spaces of the periodic table. The name "isobare" (*Gk.* equal weight) was suggested by Stewart in 1918.[87] When a β-ray change occurs, the new element occupies a space one forward in the periodic table from the space proper to its parent. Since the loss of an electron as a β-ray has practically no effect upon the mass of an atom, the new element is an isobare of the first. Isobares, though scarce, are also found among the non-radioactive elements. For example, an isotope of calcium has atomic weight 40, and is, therefore, an isobare of the isotope of argon possessing the same mass.

30. Influences of the Nucleus upon Atomic Properties

It is important to distinguish as clearly as possible between (*a*) the mass, and (*b*) the charge of an atomic nucleus, in relation to the properties of the atom as a whole.

(*a*) The mass of the nucleus accounts for the mass of the atom, and the theory of isotopes shows that it may be always expressed in terms of a whole number. Since the negative electrons in an atom are relatively so light, the mass of an atom is due to the *number of protons in its nucleus*. Atoms possessing the same weight must, therefore, have the same number of protons in their nuclei.

(*b*) The charge of the nucleus defines the position of the atom in the periodic table. It is also a whole number, equal to the atomic number. Atoms possessing the same nuclear charge have also the same number of extranuclear electrons, since the atom as a whole is neutral, so that this number is also equal to the atomic number of the elementary atom.

On the above basis, it is possible to explain the chemical and spectral similarity of isotopes. When two atoms have the same nuclear charge but different atomic weights, they have the same number of extranuclear electrons, but a different number of protons in their nuclei. The former fact then explains the resemblance of isotopes, *if chemical and spectroscopic properties depend upon the extranuclear system*. The radioactive properties of isotopes will be different, because they possess different nuclei. This explanation harmonizes with the group displacement law (see next section). It is not difficult to imagine that two atoms may differ in their nuclei, but yet have the same outer system of electrons, so that all properties governed by the latter are the same. Such isotopes may be expected to have the same atomic volume but different density.

It is necessary to inquire how it happens that atomic nuclei may have different masses and yet bear equal charges. It is only possible to account for this by assuming that such nuclei contain electrons in addition to the protons which account for their mass. In considering the uranium atom, it was found necessary to include negative charges in the nucleus. Considering the two isotopes of neon from this point of view, the atomic weights are 20 and 22 respectively, and the atomic number is 10, so that the charge on the nucleus of each kind of atom is 10, referred to the electronic charge as unity. If the atom of one isotope has a nucleus containing 20 protons and 10 electrons,

then the resultant nuclear charge is 10 units, and the mass of the atom (due to the protons) is 20 units. In the same way, if the atomic nucleus of the other isotope contains 22 protons and 12 electrons, the resultant charge is again 10 units, but the mass is now 22 units. These results may be tabulated as follows :—

TABLE III

The Isotopes of Neon

	Neon (20).	Neon (22).
Number of protons in nucleus = P .	20	22
Number of electrons in nucleus = E .	10	12
Net nuclear charge = $P - E = Z$.	10	10
Number of extranuclear electrons = Z	10	10
Mass of the atom = P . . .	20	22

Isobares can be explained in an analogous fashion. If two atoms have the same weight and different charges, they have the same number of nuclear protons, but a different number of extranuclear electrons. According to Aston and Dempster, the two isotopes of argon, atomic number 18, have atomic weights 38 and 40, and the two isotopes of calcium, atomic number 20, have atomic weights 40 and 44.[88] The isotope of argon of mass 40 must have 40 protons in its nucleus associated with $40 - 18 = 22$ negative electrons so that the resultant nuclear charge shall be 18. Similarly, the isotope of calcium of mass 40 will have 40 protons and 20 electrons in its atomic nucleus. These results are collected in the following table :—

TABLE IV

The Isobares of Argon and Calcium

	Argon (40).	Calcium (40).
Number of protons in the nucleus = P	40	40
Number of electrons in the nucleus = E	22	20
Net nuclear charge = $P - E = Z$.	18	20
Number of extranuclear electrons = Z	18	20
Mass of the atom = P . . .	40	40

The relationship $P = E + Z$ gives the value of E in all cases, since P and Z are known. Isobares are very much more common in the radioactive series, where similar explanations may be advanced. The rareness of occurrence of isobares among the non-radioactive elements is somewhat striking, and, indeed, one of the points which awaits full explanation is the fact that, when so many possible arrangements can be worked out on paper, only a very limited number of these appear to be realized in practice.

It is noteworthy that isotopes do not always differ in atomic weight, although they must be characterized as different on account of varying radioactive behaviour. Such "isobaric isotopes" may be explained by "nuclear isomerism." Their nuclei contain equal numbers of protons and electrons, and their different speeds of disintegration may depend on different arrangements. An example of such isomerism is provided by radium D and actinium B. Each has atomic number 82, and atomic weight 210.

Neuburger has distinguished between four classes of isotopes.[39] For instance, a somewhat different case appears to be provided by uranium Y and ionium, which are produced from the same parent uranium II by the same kind of change, i.e., by the loss of an α-particle. Meitner has suggested that two kinds of α-ray change can occur, depending on whether the α-particle was or was not "neutralized" by negative electrons in the nucleus before emission. Thus she has distinguished between the condition of α-particles in radioactive nuclei, so that there may be a certain number of one kind, and others of a different kind. The products of simultaneous changes of this sort may be regarded as isotopes in a special sense.

The terms "heterobares" and "heterotopes" are sometimes met with in literature relating to isotopes. They refer to atoms having unequal atomic weights and unequal atomic numbers respectively.

These considerations increase the difficulty of defining an element.[40] It is incorrect to say that an element is that which cannot be broken up into anything simpler. Nor can the electron be regarded as a chemical element, as Ramsay once suggested. Moreover, the idea of regarding each isotope as a separate element must be abandoned, although different names have been given to isotopes in the radioactive group, for this would give the word "element" a meaning never previously attached to it. Lastly, since isotopes exist, an element cannot

be defined as that which has fixed atomic weight. The definition of an element should, therefore, contain the idea of constancy of atomic number. This emphasizes the dependence of chemical properties on nuclear charge.

It may seem that the nuclei described would not possess much stability, since positive electrons are placed in close proximity to each other. At these minute distances, however, it has already been suggested that the ordinary "inverse square" law of repulsion between like charges may break down. It is also possible that the electrons may be so placed as to hold the protons together.

This section may be conveniently concluded by a brief summary of the leading deductions made in it. On the nuclear theory of the atom, radioactivity and atomic weight are attributed to the nucleus, and chemical and spectroscopic characteristics to the outer electrons. The mass and charge of the nucleus are whole numbers. The mass of the nucleus has little influence on chemical properties and on spectra. It is necessary to postulate the presence of negative electrons in nuclei in order to account for isotopes and isobares. The possibility of nuclear isomerism has been indicated. An atom contains protons and electrons only.

The reader is recommended to consult the Royal Society discussion on isotopes,[41] also the list of isotopes (1923).[42]

31. Radioactive Elements and the Periodic Law

The "Group Displacement Law" was enunciated by Fajans and Soddy in 1913 before the significance of atomic number was fully appreciated.[43] It is conveniently interpreted, however, by Moseley's results.

The α-particle carries a mass of 4 units on the ordinary atomic weight scale, and its loss by an atom causes a decrease in atomic weight of this amount. A β-particle, on the other hand, is an electron whose "atomic weight" on the same scale is 0·00054, so that its removal causes no appreciable change in atomic weight. Thus, the product of an α-ray change will occupy an earlier position in the periodic table than its parent.

These changes may now be examined from the point of view of changes in nuclear charge. It has been pointed out (section 8) that a monovalent ion in solution carries a charge of one electron, a bivalent ion of two, and so on. Thus the atom of an element in Group II of the periodic table is bivalent, and possesses tw

"valency electrons," with which it can part company when it becomes a doubly-charged positive ion, similar considerations holding in the other groups. Now, when an atom loses an α-particle (which carries two positive charges), its capacity of carrying valency electrons is lessened by 2. The new atom should, therefore, fall into a group two earlier than that of its parent. The loss of a β-particle, on the other hand, corresponds with an increase of one unit of positive charge, so that the new atom can in this case carry one more valency electron, and it falls into a group one higher than that of the atom which produced it. These deductions are in conformity with the experimental results.

This may also be considered from the point of view of atomic numbers. The α-particle must arise from a radioactive nucleus, and carry away two positive charges. This evidently corresponds with a reduction in atomic number of two units, and involves the result that an atom produced by α-ray change falls into a group two behind its parent in the periodic system. Similarly, the loss of a β-ray leaves the nucleus positively charged, and, therefore, the new atom has an atomic number one greater than its parent, and occupies a position in the group immediately following. Thus, it has been shown that the emission of α-rays by radium leaves it negatively charged.[44]

The following table illustrates how the displacement law works in an actual case :—

TABLE V

Example of the Displacement Law

	Thorium A.	α-Ray. ⟶	Thorium B.	β-Ray. ⟶	Thorium C.
Atomic weight . .	216		212		212
Atomic number . .	84		82		83
Periodic group . .	VI		IV		V

Soddy and Darwin have drawn up convenient tables illustrating these relationships.[45]

The importance of the displacement law has chiefly lain in the assistance it has given in the matter of deciding the atomic weights and atomic numbers of members of radioactive chains, once it had been proved in a sufficiently large number of cases to justify such generalizations. Some of these elements possess such short lives that investigation of these constants by direct means would be difficult, if not impossible. The law has also

led to the discovery of new elements, such as uranium X_2, identified by Fajans. The idea has also been applied with some success to the non-radioactive elements.[46]

It has been observed that an α-ray change is frequently followed by two β-ray changes in succession, and it may be supposed that an α-ray change leaves two negative electrons in excess, which are emitted in the two following successive changes. Meitner explains the branching in radioactive chains (where an atom undergoes an α- and β-ray change simultaneously) as follows. The α-ray change followed by two β-ray changes constitutes a series of three, which may not, however, take place in this order. If a β-ray is first emitted, then successive transformations can be either an α-ray change followed by a second β-ray change, or a β-ray change followed by an α-ray change, thus :—

$$\text{Thorium B} \xrightarrow{\beta} \text{Thorium C} \begin{cases} \xrightarrow{\beta} \text{Thorium C}' \xrightarrow{\alpha} \\ \xrightarrow[\alpha]{} \text{Thorium C}'' \xrightarrow[\beta]{} \end{cases} \text{Thorium D.}$$

Similar branching occurs at radium C and actinium C. As already noted, Meitner further distinguishes between two classes of helium nuclei present in radioactive atoms, which differ in respect of neutralization by negative electrons.[47] Thus an α-particle or helium nucleus may be neutralized by being associated with two negative electrons. Helium nuclei may be expelled until a neutralized helium nucleus becomes unstable, when the three changes explained above may occur.

In the present chapter, the *numbers* of protons and electrons in different atoms have been considered, and the *arrangements and movements* of these units is reserved to later chapters, which deal specially with the architecture of the atom.

REFERENCES: (V)

See Nos. 3, 8, *and* 20 *in Bibliographical List at end of book.*

1 (p. 100) O. W. Richardson : "The Emission of Electrons from Tungsten at High Temperatures: an Experimental Proof that the Electric Current is carried by Electrons"; *Phil. Mag.*, 1913; (vi.) **26**, 345.

2 (p. 102) A. van den Broek: "Die Radioelemente, das periodische System und die Konstitution der Atome"; *Phys. Z.*, 1913; **14**, 32.

3 (p 103) C. G. BARKLA: "The Spectra of the Fluorescent Röntgen Radiations"; *Phil. Mag.*, 1911; (vi.) **22**, 396.
C. G. BARKLA and J. NICOL: "X-Ray Spectra"; *Phil. Mag.*, 1910; (vi.) **84**, 139.
4 (p. 103) M. SIEGBAHN: "Sur l'existence d'un nouveau groupe de lignes (série M) dans les spectres de haute frequence"; *Compt. Rend.*, 1916; **162**, 787.
5 (p. 103) V. DOLEJŠEK: "On the N Series in X-Ray Spectra"; *Nature*, 1922; **109**, 582: *Z. Physik*, 1922; **10**, 129.
6 (p. 104) C. G. DARWIN: "Collision of α-Particles with Light Atoms"; *Phil. Mag.*, 1914; (vi.) **27**, 299.
7 (p. 104) E. RUTHERFORD: "The Scattering of α- and β-Particles by Matter, and the Structure of the Atom"; *Phil. Mag.*, 1911; (vi.) **21**, 669.
8 (p. 105) H. GEIGER and E. MARSDEN: "The Laws of Deflexion of α-Particles through Large Angles"; *Phil. Mag.*, 1913; (vi.) **25**, 604.
9 (p. 105) E. RUTHERFORD and J. M. NUTTALL: "The Scattering of α-Particles by Gases"; *Phil. Mag.*, 1913; (vi.) **26**, 702.
10 (p. 105) C. G. BARKLA: "Energy of Scattered X-Radiation"; *Phil. Mag.*, 1911; (vi.) **21**, 648.
11 (p. 105) *Idem*: "Secondary Radiation from Gases subject to X-Rays"; *Phil. Mag.*, 1903; (vi.) **5**, 685: 1904; (vi.) **7**, 543.
12 (p. 105) J. J. THOMSON: "Conduction of Electricity through Gases"; 1906; p. 321. (2nd edition, Cambridge University Press.)
Idem: "The Number of Corpuscles in an Atom"; *Phil. Mag.*, 1906; (vi.) **11**, 769.
13 (p. 105) O. LODGE: "Electrons, or the Nature and Properties of Negative Electricity"; 1906; p. 151. (G. Bell and Sons, Ltd.)
14 (p. 106) H. J. G. MOSELEY: "The High Frequency Spectra of the Elements"; *Phil. Mag.*, 1913; (vi.) **26**, 1024; 1914; (vi.) **27**, 703.
15 (p. 108) D. COSTER and G. HEVESY: "On the New Element Hafnium"; *Chem. and Ind.*, 1923; **42**, 258. See also *ibid.*, pp. 764, 784.
16 (p. 109) J. CHADWICK: "Charge on the Atomic Nucleus, and the Law of Force: Validity of the Inverse Square Law for the Platinum Atom"; *Phil. Mag.*, 1920; (vi.) **40**, 734.
17 (p. 111) E. RUTHERFORD and F. SODDY: "Note on the Condensation Points of Thorium and Radium Emanations"; *J. Chem. Soc., Proc.*, 1902; **18**, 219. See also *Phil. Mag.*, 1903; (vi.) **5**, 561.
S. KINOSHITA: "Condensation of the Actinium and Thorium Emanations"; *Phil. Mag.*, 1908; (vi.) **16**, 121.
18 (p. 111) B. B. BOLTWOOD: "Note on a new Radioactive Element"; *Amer. J. Sci.*, 1907; (iv.) **24**, 370. See also *ibid.*, 1906; (iv.) **22**, 537.
19 (p. 111) W. MARCKWALD and B. KEETMAN: "Notiz über das Ionium"; *Chem. Ber.*, 1908; **41**, 49.
B. KEETMAN: "Über Ionium"; *Jahr. Rad. Elekt.*, 1909; **6**, 265.
20 (p. 111) C. A. VON WELSBACH: "Über die chemische Untersuchung der Aktinium enthaltenden Ruckstände der Radiumgewinnung"; *Z. anorg. Chem.*, 1911; **69**, 353.
21 (p. 111) O. HAHN: "Eine Neues Zwischenprodukt im Thorium"; *Phys. Z.*, 1907; **8**, 277. See also *ibid.*, 1908; **9**, 245.
22 (p. 111) W. MARCKWALD: "Zur Kenntnis des Mesothoriums"; *Chem Ber.*, 1910; **43**, 3420.

22 (p. 111) F. SODDY: "The Chemistry of Mesothorium"; *J. Chem. Soc., Trans.*, 1911; **99**, 73.

23 (p. 111) J. ELSTER and H. GEITEL: "Beitrage zur Kenntnis der Radiaktivität des Thoriums"; *Phys. Z*, 1906; **7**, 445.

G. A. BLANC: "Radioactivity of Mineral Springs"; *Phil. Mag.* 1905; (vi.) **9**, 148.

B. BOLTWOOD: "On the Radioactivity of Thorium Salts"; *Amer. J. Sci.*, 1907; (iv.) **24**, 93.

24 (p. 111) F. SODDY: "Chemical Relationships of the Radio-elements"; *Chem. Soc. Annual Report,* 1910; **7**, 285. See also *ibid.*, 1913; **10**, 262.

25 (p. 112) F. SODDY and H. HYMAN: "The Atomic Weight of Lead from Ceylon Thorite"; *J. Chem. Soc., Trans.*, 1914; **105**, 1402.

26 (p. 112) T. W. RICHARDS and C. WADSWORTH: "Further Study of the Atomic Weight of Lead of Radioactive Origin"; *J. Amer. Chem. Soc.*, 1916; **38**, 2613.

27 (p. 112) A. S. RUSSELL and R. ROSSI: "An Investigation of the Spectrum of Ionium"; *Proc. Roy. Soc.*, 1912; **A87**, 478.

28 (p. 112) E. RUTHERFORD and E. N. DA C. ANDRADE: "The Wave-Lengths of the Soft γ-Rays from Radium B"; *Phil. Mag.*, 1914; (vi.) **27**, 854.

29 (p. 112) M. SIEGBAHN and W. STENSTRÖM: "Sur les spectres des rayons X des élémentes isotopes"; *Compt. Rend.*, 1917; **165**, 428.

30 (p. 112) W. D. HARKINS and L. ARONBERG: "The Spectra of Isotopes, and the Vibration of Electrons in the Atom"; *Proc. Nat. Acad. Sci.*, 1917; **3**, 710. See also *J. Amer. Chem. Soc.*, 1920; **42**, 1328

L. ARONBERG: "Note on the Spectrum of the Isotopes of Lead"; *Astrophys. J.*, 1918; **47**, 96.

31 (p. 112) T. R. MERTON: "On the Spectra of Lead Isotopes"; *Proc. Roy. Soc.*, 1921; **A100**, 84.

32 (p. 112) P. EHRENFEST, N. BOHR: "The Difference between Series Spectra of Isotopes"; *Nature*, 1922; **109**, 745: **110**, 37.

33 (p. 113) A. KRATZER: "Eine spektroscopische Bestätigung der Isotopen des Chlors"; *Z. Physik*, 1920; **3**, 460.

F. W. LOOMIS: "Infra-Red Spectra of Isotopes"; *Astrophys. J.*, 1920; **52**, 248.

34 (p. 113) F. W. ASTON: "The Mass Spectra of the Chemical Elements" (Parts I to VI); *Phil. Mag.*, 1920; (vi.) **39**, 611: (vi.) **40**, 628: 1921; (vi.) **42**, 140: 1923; (vi) **45**, 934: 1924; (vi.) **47**, 385: 1925; (vi.) **49**, 1191.

Idem: "The Mass Spectra of the Alkali Metals"; *Phil. Mag.*, 1921; (vi.) **42**, 436.

35 (p. 114) E. KOHLWEILER: "Anreicherung der leichteren Isotopen des Jods"; *Z. Phys. Chem.*, 1920; **95**, 95.

36 (p 114) J. N. BRÖNSTED and G. VON HEVESY: "The Separation of the Isotopes of Mercury"; *Nature*, 1920; **106**, 144: *Phil. Mag.*, 1922; (vi.) **43**, 31.

37 (p. 114) A. W. STEWART: "Atomic Structure from the Physico-chemical Standpoint"; *Phil. Mag.*, 1918; (vi.) **36**, 326.

38 (p. 116) A. J. DEMPSTER: Positive Ray Analysis of Potassium, Calcium and Zinc"; *Phys. Rev.*, 1922; (ii.) **20**, 631.

39 (p. 117) M. L. NEUBURGER: "The Isotopy of the Radioelements"; *Nature*, 1921; **108**, 180.

40 (p. 117) F. PANETH: "Über den Element- und Atombegriff in Chemie und Radiologie"; *Z. Phys. Chem.*, 1916; **91**, 171.

41 (p. 118) Discussion on Isotopes; *Proc. Roy. Soc.*, 1921; **A99**, 87.
42 (p. 118) International Table of Isotopes and Radioactive Constants; *Chem. and Ind.*, 1923; **42**, 175.
43 (p. 118) F. SODDY: "Radioactivity"; *Chem. Soc. Annual Report*, 1913; **10**, 262.
K. FAJANS: "Die Stellung der Radioelemente im periodischen System"; *Phys. Z.*, 1913; **14**, 136. See also *ibid.*, p. 131, and A. S. RUSSELL; *Chem. News.*, 1913; **107**, 49, and section 9 of G. VON HEVESY; *Phil. Mag.*, 1913; (vi.) **25**, 411.
44 (p. 119) P. CURIE and (Mme.) CURIE: "Sur la charge éléctrique des rayons déviables du radium"; *Compt. Rend.*, 1900; **130**, 647. See also R. J. STRUTT: "An Experiment to exhibit the loss of Negative Electricity by Radium"; *Phil. Mag.*, 1903; (vi.) **6**, 588.
45 (p. 119) F. SODDY: "The Conception of the Chemical Element as enlarged by the Study of Radioactive Change"; *J. Chem. Soc., Trans.*, 1919; **115**, 1.
C. G. DARWIN: "The Structure of the Atom"; *Nature*, 1920; **106**, 51, 81. See also A. S. RUSSELL: "Radioactive Disintegration Series, and the relation of Actinium to Uranium"; *Phil. Mag.*, 1923; (vi.) **46**, 274.
46 (p. 120) A. S. RUSSELL: "A Calculation of the Atomic Weights of Isotopes"; *Nature*, 1923; **112**, 588.
Idem: "The Complexity of the Elements. Part I. Elements of odd Atomic Number"; *Phil. Mag.*, 1924; (vi.) **47**, 1121.
47 (p. 120) L. MEITNER: "Über die verschiedenen Arten des radioaktiven Zerfalls und die Möglichkeit ihrer Deutung aus der Kernstruktur"; *Z. Physik*, 1921; **4**, 146.

CHAPTER VI

RADIANT ENERGY

32. The Forms of Radiant Energy

IN this chapter the position in regard to knowledge of the way in which energy transmits itself through space is considered, more particularly in relation to those facts and theories which bear upon the question of atomic structure.

When light comes to us from the sun, it is well known that it travels through about ninety million miles in a few minutes without in any way permanently affecting the medium. It may be stated at once that no one knows at present exactly how this happens. It is an outstanding problem of physics which is still unsolved. At the same time, it is possible that physicists are at the present time near to the solution, and, if they seem further away on account of recent discoveries, this is probably due to the fact that the nature of the difficulties which stand in the way are much better appreciated.

The theories which have been proposed to account for this phenomenon may now be briefly considered. In ancient times, light was thought by some philosophers to be a property of the eye. This is, of course, completely disproved by the fact that a photographic plate is also susceptible to it. Another ancient theory was that the sun emitted particles of some kind, which, by their impact on the eye, caused the sensation of light. Newton was a staunch advocate of the "corpuscular" theory. This encountered so many difficulties that it was ultimately abandoned. For example, it failed to explain satisfactorily the simultaneous reflection and refraction of light at the boundary of a material medium, though Newton's suggestion of "fits" of easy reflection and easy transmission was certainly ingenious. The corpuscular theory passed out of fashion when Foucault showed that light travelled more slowly the denser the medium, whereas it can be demonstrated without much difficulty that

the corpuscular theory demands that the opposite should occur. This theory, moreover, was incapable of explaining interference phenomena. It was found that light of all colours travelled with the same speed, and an æther-wave theory was next proposed. If waves were transmitted through space, it seemed necessary to assume the existence of a quasi-elastic medium, generally known as the "æther." This medium was supposed to possess properties different from those met with in matter, and to extend indefinitely throughout space.

According to the wave-theory, light of a definite colour possesses a fixed wave-length. If c is the velocity of light *in vacuo*, and λ the wave-length of a particular colour, then c is evidently given by the relation—

$$c = \lambda\nu \quad . \quad . \quad . \quad . \quad (1)$$

where ν is the number of waves passing a given spot in unit time, otherwise called the "frequency" of the wave. Now, if a difference in wave-length exists, different angles of refraction for light of different colours would be anticipated. This is what is actually observed when "white" light forms a spectrum by passing through a glass prism. The red rays are least deviated, and consist of waves of greatest length, and, therefore, of smallest frequency. The violet rays, on the other hand, are *most deflected, and consist of waves of smallest length and* greatest frequency, other colours occupying intermediate positions. Now, red rays and the invisible "infra-red" rays, like those of light, excite the sensation of heat, and are dispersed by a prism in a similar way. Heat and light rays thus possess a similar character, the former possessing greater wave-length. Hertz showed that the velocity of electric waves was the same as the velocity of light, and that their behaviour could be explained on the assumption that they were of the same nature, but possessed greater wave-length.[1] The properties of X-rays, on the other hand, suggest that they are also of the same nature as light rays, but have a smaller wave-length. They exhibit, for example, the property of diffraction in common with light rays, but to a less extent (p. 58).

Thus all forms of radiant energy fall into line as one phenomenon. After having postulated an all-pervading æther to account for the transmission of light, it would have complicated matters considerably if it had been necessary to imagine another medium for the propagation of other forms of radiant energy, such as electromagnetic energy. Fortunately, however, this is

unnecessary, and the properties with which we must endow the æther for light transmission are also those necessary to explain the passage of electrical disturbances through space. All forms of radiant energy are, according to this theory, æthereal waves, which differ only in wave-length and, therefore, in frequency, and travel with the velocity of light. For each of them the relation (1) holds, c being constant and equal to about 3×10^{10} cms., or 187,000 miles per second, so that the length of a wave is always inversely proportional to the frequency, the constant of proportionality being the velocity of light. The "wave-number" w is the reciprocal of the wave-length, and is, therefore, a measure of frequency. The "period" of a wave p is the time taken to execute one complete wave-length, so that it is equal to the reciprocal of the frequency ν. This gives—

$$w\lambda = \nu p = 1 \qquad (2)$$

For purposes of comparison, Table VI shows the approximate limits of the values of λ for different forms of radiant energy. A millimicron (written $\mu\mu$) is a millionth of a millimetre. The numbers given in these units must be multiplied by 10 to express them in Ångstrom units (Å.U. $= 10^{-8}$ cm.).

TABLE VI

Limits of Wave-Length for Different Forms of Energy

X-rays	0·01 to 0·1 $\mu\mu$
Ultraviolet light	100 to 400 $\mu\mu$
Visible light	400 to 800 $\mu\mu$
Heat	1000 to 10,000 $\mu\mu$
Electric waves	4 mms. to 1000 kilometres

The biggest gap in the complete spectrum of waves would thus appear to lie between X-rays and the shorter ultraviolet rays. Intermediate waves have, however, been realized experimentally.[2] The fact that the different waves merge into each other makes it easier to understand that they are qualitatively of the same kind.

33. Electric and Magnetic Induction

The idea of "lines" of electric and magnetic force was introduced by Faraday.[3] It is well known that when iron filings are dusted round a magnetic pole, they tend to take u

chain formations of a regular character. Similarly, Faraday showed that the field of a charged conductor is external, and *may be imagined to consist of lines or tubes, any one of which* marks out the direction of electric force along it. According to more recent views, frictional electrification, which produces two equal charges of opposite sign, is caused by the removal of negative electrons, which leaves behind an equal number of positively charged atoms. An electron may be regarded as having imaginary lines of force proceeding from it in all directions. Since there is no observed production of one kind of electricity without the other kind, the lines of force proceeding from a charged body will end somewhere at points where equal and opposite charges exist, perhaps on the walls of the room. Such is the general conception of an electrostatic field. A current of electricity is to be thought of as the movement of electrons with constant average velocity accompanied by a corresponding moving external field. Now, if a current is passed through a vertical wire on which a piece of paper dusted with iron filings has been threaded, it is found that the filings tend to arrange themselves in circles round the wire, proving the presence of a magnetic field. Thus the movement of lines of electric force "induces" lines of magnetic force, in such a way that the two kinds of lines passing through any given point are mutually at right angles. The lines of electric force are radial from the wire carrying a current, while the magnetic lines are in the form of closed curves round its path. In similar fashion, the movement of lines of magnetic field may be shown to be accompanied by induced lines of electric force, and the conclusion is reached that though electric and magnetic fields may exist independently of each other when at rest, inductive effects are produced when either kind of field is in motion.

The phenomena relating to induced currents are generally well known, so that a brief reference here will suffice. Consider two parallel wires; the first, or "primary," has its ends connected through a battery and a key by which the circuit can be made or broken, and the other, or "secondary," wire forms part of a different circuit containing a galvanometer. Then it is found that although nothing is observable in the secondary circuit when a steady current passes through the primary, a momentary current is indicated in the secondary circuit by the galvanometer when the battery circuit is made or broken. When the primary circuit is broken, the induced current in the secondary is in the same direction as that in the primary before

break, and when the current is made, it is in the opposite direction. This result is evidently due to some action in the space between the two circuits. The question arises as to whether the effect is instantaneous or not. Hertz showed that the experimental results were consistent with the view that any effects due to modifications in the electric and magnetic fields at any point were transmitted with the velocity of light. This applies, not only to the ordinary inductional effects, which are of predominating importance at small distances, but also to the radiational effects, which become relatively more important at large distances. In his classical experiments, the radiational effects were investigated. If two brass knobs, placed a short distance apart and joined to two large spheres to give them greater capacity, are connected with the poles of a powerful induction coil, discharge occurs by means of sparks between the knobs. When the vibrator is working well, sparks can be taken from pieces of metal, whether insulated or not, contained in the same room. Hertz used a "resonator" consisting of a wire bent into circular shape, on one end of which a small brass knob was placed, the other being provided with a point, whose distance from the knob could be varied. Sparks which decreased in length as the resonator and vibrator were separated to greater distances were obtained in this gap. A stone or brick wall or a door interposed did not stop the effect, but suitable metallic screens did so, because the radiation was reflected by them, as Hertz was able to prove. When reflection occurs, "stationary" waves are set up, having "nodes" at regular distances. Hertz found that when the period of the vibrator was about one-thirty millionth of a second, the interval between the nodes was about five metres. This distance was equal, according to the wave-theory, to half the wave-length of the original radiation, which, in this case, was ten metres. Thus, $c = \lambda/p = 300{,}000$ kilometres, or 3×10^{10} cms. per second, which is the velocity of light. The experiments of Hertz were confirmed by Trouton.[4]

Consider now the inductive effects of an electron in motion. When at rest, the electron has an electrostatic field, and when moving, a magnetic field is set up. Thus the effect of an applied E.M.F. is to give the electrons in a circuit kinetic energy, and at the same time to create the magnetic field. Now, if an electron at rest is caused to move with uniform velocity under a steady E.M.F., there must be a brief interval of time during which it is acquiring this velocity, when it is being accelerated.

When an electron is undergoing acceleration, a wave is emitted, according to the experiment described at the commencement of the previous paragraph. In harmony with classical electromagnetic theory, *the accelerations of electrons are responsible for the production of electric waves.*

The above considerations throw light on what happens when electrons undergo vibratory movements. Consider a single electron executing simple harmonic motion. At the ends of its path, its kinetic energy is zero, and the electric field reaches its maximum value. In the central position, however, the kinetic energy is at a maximum, so that the magnetic field attains its maximum value also. The maximum of one kind of field corresponds with the minimum of the other kind, and when one is increasing, the other is decreasing. The acceleration directed to the centre will be responsible for the emission of an electromagnetic wave. The characteristics of the wave will be such that the electric and magnetic fields are at right angles at any point upon the "wave-front," and the period of the wave will be that of the electron. If such a wave falls upon an electron, it can excite vibration in it corresponding with its own frequency. This kind of wave motion constitutes radiant energy, according to the electromagnetic theory of light.

It will be clear in the case cited above that unless the energy of the electron is maintained in some way, it will gradually approach the central position, where it will come to rest. Similarly, an electron tending to move in a circle but having an acceleration directed to the centre will radiate energy, meanwhile approaching the central position. Thus its path is actually spiral, and radiation ceases when it come to rest. If, however, it is moving in a straight line, and suddenly stopped by an obstacle, a series of waves will spread out in spherical form from the point of impact. This explanation was adopted by Stokes for the production of X-rays by the stoppage of the cathode ray particle.

The electromagnetic theory of light was successful, in the hands of Maxwell, in explaining many known experimental facts, and in predicting facts which were later verified.[5] His famous differential equations led to the following conclusions :—

(1) *The refractive index of a medium is equal to the square root of the dielectric constant.* This was verified for a large number of substances, but many discrepancies occurred. Most of these, however, were satisfactorily interpreted when the idea of electrons was introduced. There are certain special cases

which Thomson has explained by means of "intramolecular ionization."[6] (Section 53.)

(2) *The velocity of light can be expressed as equal to the number of electrostatic units in the electromagnetic unit of quantity of electricity.* This has also been verified. Thus the ratio between the two values of the electronic charge given in Table II (p. 38) is 3×10^{10}, which is the velocity of light in centimetres per second.

Rayleigh used the theory to explain the equations of Fresnel relating to the velocity of light in crystalline media, and thus another notable piece of evidence was obtained for its truth. These facts, together with the proof of the existence of electric waves by Hertz in 1889, and the demonstration that they moved with the velocity of light, tended to place the theory upon a strong basis. Maxwell's view, then, was that light consisted of transverse electromagnetic waves, which were characterized by two "vectors" at right angles, one corresponding with the electric, and the other with the magnetic character of the disturbance.

In spite of the successes of the electromagnetic theory mentioned above, it appears to fall short in explaining other experimental results. Of these, the following may be mentioned: (1) The distribution of energy among the various wave-lengths emitted by a "black" body; (2) the phenomena connected with the photoelectric effect; (3) the origin of the line spectra of elements. These matters will now occupy attention, except the last, which must be deferred to Chapter VIII, where the Bohr atomic model is considered (section 46).

34. Isothermal Radiation

It is well-known that a black surface is more efficient than any other in absorbing incident radiation. The limiting case would be found in a perfectly "black" body, which would entirely absorb incident radiant energy. Such a body is never realized in practice. It would reflect, transmit and scatter no energy, but would radiate perfectly. For such a body, the radiation emitted at a given temperature would be a maximum, and Kirchoff showed that its intensity corresponding to a given frequency depended only on the frequency and the absolute temperature, thus:

$$K_\nu = f(\nu, T) \quad . \quad . \quad . \quad (3)$$

which means that the intensity K_ν of frequency ν is some function of ν and T the absolute temperature. Considering a continuous spectrum of radiation having frequencies from $\nu = 0$ to $\nu = \infty$, emitted by unit area of a black body in unit time in a given direction, and selecting any small frequency interval $d\nu$ containing the range of frequencies between ν and $\nu + d\nu$, the energy E_ν or "emissivity" of this radiation is given by Planck as follows :—

$$E_\nu = 2\pi K_\nu d\nu \quad . \quad . \quad . \quad (4)$$

The form of the function expressed in equation (3) remained for some time unknown, though it was of considerable interest and importance to physicists. Experimental evidence could not be obtained until it became possible to construct a black body sufficiently near to the ideal condition for the purpose. The researches of Lummer, Wien, Jahnke, Pringsheim, and Kurlbaum were made on the basis of a suggestion of Kirchoff, which was embodied in the "Law of Cavity Radiation."

An opaque enclosure is made, having a small opening. If radiation falls upon this opening, and enters the enclosure, it will suffer a certain amount of reflection when it strikes the interior wall, since the latter is not perfectly "black." The reflected radiation will be again reflected at some other part of the interior, the process being indefinitely repeated. At each reflection, however, an ever-increasing amount of radiation will be left unabsorbed, so that after a sufficiently large number of reflections, practically all the incident energy will have become absorbed within the enclosure. The small amount reflected back through the small opening may be neglected for practical purposes. Thus the radiation emitted from an isothermal enclosure is the same as that from a black body. If, now, this body is placed within a bath at constant temperature, a condition of "isothermal equilibrium" is eventually attained, in which the continual exchange of energy between the walls and the space inside the enclosure is such that the walls lose as much as the space gains at any moment, and vice versa. In these circumstances, a thermometer placed in different parts of the interior shows that the distribution of temperature is uniform.

The radiation within the enclosure can be studied by opening a small window in the walls, and by receiving the emitted energy in a dispersing apparatus. This causes the different wave-lengths present to be refracted to varying extents, and if a suitable receiving instrument is placed at different parts of

the spectrum, it becomes possible to determine in what way the energy is distributed between the waves of different "colours." Such an instrument is the "bolometer," introduced by Langley in 1881, which has largely replaced the thermopile in investigating radiation.[7] It depends upon the "Wheatstone Bridge" principle. Two of the corresponding "arms" consist of very thin, short strips of metal. When one of these arms becomes warmed by radiation, its resistance rises, and the state of balance in the bridge is upset. The current passing through the galvanometer is related to the rise in temperature in the arm, and from this the energy received is calculated. By such means, a curve is obtained connecting intensity of energy and wave-length, for a given temperature of the enclosure. Fig. 19 shows a series of curves obtained for different temperatures. It will be seen that each curve shows a marked maximum, which moves slightly in the direction of decreasing wave-length with increasing temperature. The curves rise steeply, especially at higher temperatures, and fall away again more gradually. When K_ν is plotted against ν, curves of similar type are obtained.

It must next be observed that Wien was successful in deducing a law of radiation, on the basis of thermodynamic considerations, as follows :—

$$K_\nu = C\nu^3 f\left(\frac{\nu}{T}\right) \quad . \quad . \quad . \quad (5\text{A})$$

where C is a constant. Applying Maxwell's law of the distribution of velocities among the molecules, this may be written as follows :—

$$K_\nu = \alpha\frac{\nu^3}{c^2} \cdot e^{-\frac{\beta\nu}{T}} \quad . \quad . \quad . \quad (5\text{B})$$

where c is the velocity of light *in vacuo*, e is the base of natural logarithms and α, β are constants.[8] Further, Rayleigh, on the ground of classical statistical mechanics and electrodynamics, deduced the following relation :—[9]

$$K_\nu = \frac{\nu^2}{c^2} \cdot kT \quad . \quad . \quad . \quad . \quad (6)$$

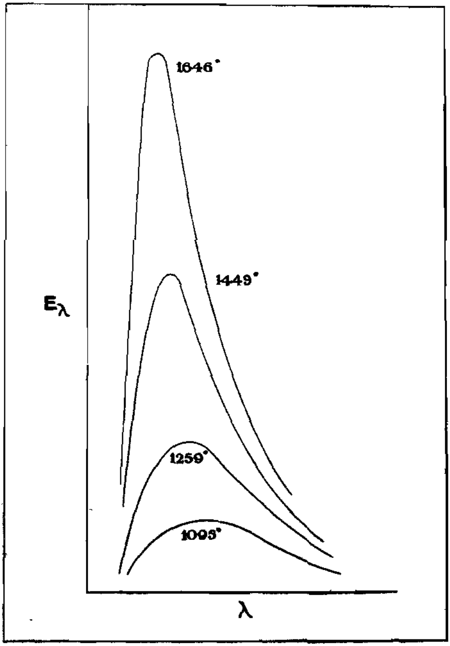
where k was given by—

$$k = \frac{R}{N} \quad . \quad . \quad . \quad . \quad (7)$$

Figure XIX

ENERGY—WAVE-LENGTH—TEMPERATURE CURVES

(*Ann. Physik*, 1901; (iv) 6, 200)



Planck's "quantum" theory of energy was introduced to account for the distribution of energy among the various wave-lengths in an isothermal enclosure, measured by *Lummer and Pringsheim and others, the results being* shown above. A maximum exists on each curve which is displaced towards the region of shorter wave-lengths with increasing temperature.

R being the familiar gas constant and *N* the Avogadro number. Now, neither equation (5) nor (6) was entirely confirmed by the experimental results. Lummer and Pringsheim showed that Wien's law was satisfactory in the region of *short* wave-lengths, but that there were systematic discrepancies in the case of *long* waves.[10] They maintained this view in spite of Planck's derivation of the law by a different and more rigorous method.[11] Nor was Rayleigh's law any more satisfactory, for it did not correspond to a maximum as observed experimentally, and while it gave a satisfactory account of the energy of *longer* waves, it failed to account for *shorter* ones. Many attempts were made to escape from this difficulty, but without success. It thus appeared that the laws of classical statistical mechanics, among which was the principle of equipartition of kinetic energy, were incapable of providing the required solution.

It was here that the " quantum " theory made its appearance. Planck was able to derive an expression which fitted the experimental results for both long and short waves, by abandoning the equipartition principle, but only by making a totally new assumption regarding the manner in which energy is absorbed or radiated by matter.[12] He supposed that the amounts of energy imparted to, or emitted by, a vibrating system could only be simple multiples of a certain fundamental amount, which depended upon the frequency of the " resonator." For example, an electron executing a definite frequency of oscillation could receive or give out one quantum of energy, or two or three quanta and so on, but not intermediate amounts. The quanta of energy are different for different resonators, and the unit quantum ε which corresponds to a frequency ν is given by—

$$\varepsilon = h\nu \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where h is Planck's universal constant. According to this view, therefore, since the period of an oscillating electron is inversely proportional to its frequency (equation (2), p. 126), an electron of short period can only emit or receive energy in relatively large quanta, whereas one of longer period can do so in smaller quanta. Thus it requires a considerable amount of energy to excite a resonator to execute high frequency vibrations, and so if very few of the available quanta have sufficient energy to excite such high frequency (corresponding to short wave-length) vibrations, the experimentally observed falling off in the energy distribution curve for short wave-lengths is explained.

In other words, according to this view, the longer waves have greater chances of being excited, other things being equal. For longer waves, the quantum is smaller and the discontinuous effect less noticeable, so that such waves behave in the manner imagined by Rayleigh. At higher temperatures, the amount of disposable energy is greater, so that the short wave-length effect is less noticeable, and the maximum is moved in their direction.

Planck's relation was derived by a statistical method based upon the above assumption. It involved a consideration of the equilibrium set up between a system of linear electromagnetic oscillators (such as, for example, bound electrons capable of vibration) and the radiation in an enclosure such as that already described. Such oscillators will only respond to waves possessing frequency equal, or nearly equal, to their own characteristic frequency. Planck then proceeded, on the basis of the quantum assumption, to distribute the available energy among the individual oscillators. This was carried out by means of probability considerations, according to which the probability of a resonator possessing a given energy is less, the greater the value of that energy relative to the mean energy at the temperature. He obtained an expression for the mean energy of an oscillator in terms of the quantum ϵ. Putting $\epsilon = h\nu$, the following radiation law was ultimately obtained :—

$$K_\nu = \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1} \qquad . \quad . \quad . \quad (9)$$

This law was first derived in 1900, and the work of numerous investigators demonstrated its validity.[13] For short waves (where $h\nu/kT$ is large) the relation passes into Wien's law, which had been confirmed for such cases. On the other hand, for longer waves (where $h\nu/kT$ is small) the formula assumes the form of Rayleigh's law, which was applicable to them, as experiment had shown. Planck's relation thus includes Wien's law and Rayleigh's law as limiting cases.

The formula of Planck has received important confirmation in other ways, which further supports the quantum theory upon which it rests. By means of experimental results, it was possible to calculate the values of the constants h and k. Planck found that $h = 6{\cdot}55 \times 10^{-27}$ (erg sec.), and $k = 1{\cdot}346 \times 10^{-16}$ (erg/deg.).[14] The dimensions of h are those of "action," or angular momentum, i.e., of energy multiplied by time. This constant is known as Planck's quantum of action. The other

constant k has the dimensions of energy, and is related to the gas constant R according to equation (7), page 132. From this the value of the Avogadro number N can be derived, and, therefore, that of the electronic charge e, according to methods explained in Chapter II. Now, R is equal to about 2 (more exactly, 1·98) calories, or $8{\cdot}31 \times 10^7$ ergs. This gives $N = R/k = 8{\cdot}31 \times 10^7/1{\cdot}346 \times 10^{-16} = 6{\cdot}175 \times 10^{23}$, a number in remarkable agreement with values obtained by quite independent methods. The corresponding value of the electronic charge e (which is not to be confused with the e of Planck's formula, the base of natural logarithms) is $e = 4{\cdot}69 \times 10^{-10}$ E.S. units.[15] Millikan's value of the same constant is $4{\cdot}774 \times 10^{-10}$ E.S. units. The agreement is remarkable, and forms strong justification for the quantum hypothesis.

The theory is, however, in complete contradiction to classical electrodynamics, by which a vibrating electron, for example, absorbs and emits energy quite continuously, and in times however small exchanges energy of correspondingly small amounts. It will shortly be seen that Einstein extended the quantum conception to the nature of radiant energy itself, in his hypothesis of "light-quanta," and that this involved a further departure from the classical wave theory of light and kindred radiations.

35. Specific Heats at Low and High Temperatures

Further evidence in support of the quantum hypothesis has been adduced from the variation of specific heats of substances with temperature. The success of the kinetic theory of gases in providing a theoretical basis for the general gas equation $PV = nRT$, and a conception of the absolute temperature of a gas as the average kinetic energy of its molecules has already been considered. Now, according to the law of equipartition of energy, a system in a state of equilibrium at temperature T possesses a mean kinetic energy of $\frac{1}{2}RT$ for each degree of freedom. A system having F degrees of freedom has, therefore, a mean kinetic energy of $\frac{1}{2}FRT$ at absolute temperature T, and the amount of heat required to raise its temperature from T to $T + 1$ (its specific heat) is given by $\frac{1}{2}FR(T + 1) - \frac{1}{2}FRT = \frac{1}{2}FR$. Further, since $R = 2$ calories (approximately), the specific heat of a system having F degrees of freedom is very nearly equal to

F calories. Since R is calculated for one gram-molecule, the specific heat of a gram-molecule of substance (at constant volume) is given approximately by F if the equipartition principle is actually a reliable guide. This quantity may be denoted by the symbol C_v.

In order to obtain theoretical values of specific heats, it becomes necessary to decide the values of F in given cases. The results obtained by experiment may now be compared with the values of specific heat given by theory in the following cases: (*a*) monatomic gases; (*b*) other gases; (*c*) solid substances.

(*a*) *The case of a monatomic gas.*—Pier has studied the molecular heat of argon up to 2350° C. by the explosion method.[16] He found the value to be constant at all temperatures, and equal to 2·98. Here there are evidently 3 degrees of freedom corresponding to the energy of translation in the three directions in space mutually at right angles. This means that effects due to vibrational or rotational energy are presumably absent. It seems difficult to imagine how this comes about, since the random collisions would be most certainly expected to communicate rotation. Here the quantum theory steps in with its suggestion that rotational energy is discontinuous. If, now, the minimum quantum of rotational energy is very large, it may so happen (since the alternatives for an argon atom are those of rotating very rapidly or not at all) that the available energy is insufficient to contribute one quantum, so that the argon atom cannot rotate. This view is supported by observations such as that of Eucken that the molecular heat of diatomic hydrogen falls to a value of 3 calories per degree below 60° absolute.[17] It appears to have lost its possibility of rotation at this temperature, a conclusion in no way to be expected from application of the equipartition principle, since pure kinetic theory does not provide for any change in the number of degrees of freedom with decreasing temperature.

(*b*) *The case of a gas whose molecules contain more than one atom.*—A diatomic gas molecule will have $F = 3$ for translational energy. If it possesses a form like that of a dumb-bell, $F = 2$ must be added for rotation in two directions at right angles, making $F = 5$ in all so far. (Rotation in the third direction at right angles is not considered, since this involves a spinning of the molecule on its axis, as a little consideration will show.) In addition, the two atoms can vibrate along the line joining them, giving $F = 2$, for one degree of freedom of vibrational kinetic energy which involves equal average potential

energy. Thus, $F = 7$, and $C_v = 7$ calories per degree.[18] Now experiment shows that the specific heat of diatomic gases is never as great as this, and, moreover, there is a considerable variation with temperature. For instance, the curve for hydrogen showing this variation is a remarkable one, having several bends. The quantum theory has been used to explain this case.[19] Of the 3 kinds of movement, translation, rotation, and vibration, the two last are periodic motions involving frequency, and may be considered in the light of the quantum theory. Considerations based on the Bohr model led to the view that the vibrational frequency was about eighteen times as great as the rotational frequency of the hydrogen molecule. Thus the rotation quantum is relatively small, and the curve showing variations in rotational energy will rise steeply at fairly low temperatures, as in the case of lead (see Fig. 21). The vibration term for hydrogen being considerably larger, the variation with temperature at low temperatures is absent, since under these conditions the available quanta are insufficient. At a certain point, however, the curve begins to rise, but more gradually, somewhat as in the case of the diamond. When the corresponding ordinates of these curves are added together, together with the constant amount due to translational energy, the resultant curve corresponds very closely indeed with experimental results. Fig. 20 shows the curve obtained by this method, the small circles showing the points obtained by experiment. This outline may serve to indicate an interesting achievement of the quantum hypothesis where classical theories break down.

Similarly, a triatomic molecule may be reckoned as having $F = 3$ (translation) and $F = 3$ (rotation), making $F = 6$. Here the molecule can rotate about three different axes at right angles. The assigning of values of F for vibration appears to be more doubtful, but in any case we need not pursue this matter further here, since classical theory is incapable of explaining the observed variation of specific heat with temperature. The " agglomeration hypothesis," supported by Benedicks and others, accounts for the decreasing number of degrees of freedom as the temperature falls by supposing that certain linkages become " anchylosed " by the effect of cooling.[20] This theory does not seem to be supported by compressibility measurements, in the case of solid bodies.[21]

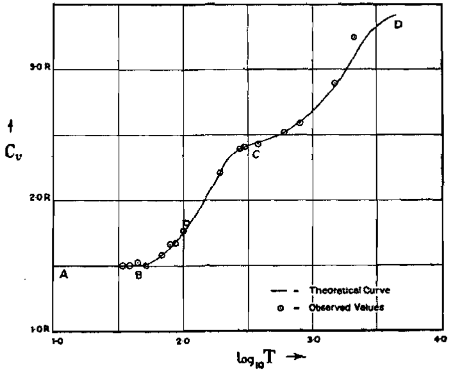
(3) *The case of solids.*—In the kinetic theory of monatomic solids, the atoms are imagined to be capable of vibratory motion about fixed centres, in simple harmonic motion. Thus $F = 3$

for the kinetic energy of vibrations in three directions at right angles, and since the potential and kinetic energies are equal for harmonic oscillations, this gives $C_v = 2 \times 3 = 6$ calories per degree. The atomic heat at constant volume is, therefore, approximately equal to the average value given by Dulong and Petit's law, which is 6·4, derived from measurements at constant pressure, and it is found that when the correction is made to

FIGURE XX

SPECIFIC HEAT-TEMPERATURE CURVE (HYDROGEN)

(*J. Chem. Soc.*, 1922; **121**, 2291)



constant volume, the agreement is a good deal closer. It is observed, however, that many elements depart widely from the law, particularly at low temperatures, where the value gradually diminishes, in some cases almost to zero. Thus, not only is the atomic heat of 6 calories departed from in many cases, but also the value varies with temperature. Here, again, the equipartition law appears to have broken down, and some other interpretation would seem to be necessary. The quantum hypothesis

has stepped into the breach with the suggestion that at low temperature only those resonators whose natural frequency is small can be caused to vibrate, the supply of available energy being small. Step by step, as the temperature is lowered, the vibrators possessing shorter periods (requiring larger quanta) will cease to vibrate, a condition being ultimately reached in which perfect stillness prevails. This state is attained by the diamond below about 40° absolute. The energy corresponding to this temperature is insufficient to supply one whole quantum to any atom, and hence the atoms remain absolutely at rest. In such circumstances, no heat is required to raise the temperature of the diamond.

In 1907, Einstein deduced an important expression for the specific heat of a solid substance at constant volume, on the basis of Planck's quantum hypothesis.[22] This expression is obtained by considering the energy of a monatomic gas as distributed among the molecules in the way indicated by Maxwell, and by examining how this energy would be imparted to a monatomic solid in contact with it. He supposed that the solid could only take up a whole number of energy-quanta, so that the atoms would have energies 0, $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$, and so on, ν being the fundamental frequency of the particular solid considered. Now for the gas, the number of molecules N_E whose energies lie between 0 and an assigned value E, the total number being N is, at temperature T, according to the integrated form of Maxwell's equation,

$$N_E = N\left(1 - e^{-\frac{E}{kT}}\right) \quad . \quad . \quad . \quad (10)$$

This corresponds to a smooth exponential curve when the number of molecules having assigned amounts of energy are plotted against these amounts. Now, if the solid absorbed energy continuously, the curve for the solid would be coincident with that of the gas. By the assumption mentioned above, however, this is not the case, and a stepped curve will be obtained, showing n_0 atoms having no energy, and $n_1, n_2, n_3 \ldots$ atoms having energies $h\nu$, $2h\nu$, $3h\nu$. . . . Further, n_0 is equal to the number of molecules of gas having energies between 0 and $h\nu$, which number is given by putting $E = h\nu$ in equation (10) above. Similarly, n_1 is equal to the number of gas molecules having energies between $h\nu$ and $2h\nu$, and so on. Thus the total energy U of the solid at temperature T is given by—

$$U = 3h\nu(n_1 + 2n_2 + 3n_3 + \ldots) \quad . \quad (11)$$

the initial 3 being introduced to include motion parallel to the three rectangular co-ordinates at right angles. The values of n_1, n_2, n_3, being substituted by means of equation (10), and the resulting series summed, an expression for U is obtained. From this, the atomic heat at constant volume, which is the change in U for a change in temperature of one degree, can be derived. This gives—

$$C_v = 3R \frac{x^2 e^x}{(e^x - 1)^2} \quad . \quad . \quad . \quad (12)$$

where x is equal to $h\nu/kT$. In this expression, when $T = 0$, $C_v = 0$, and when T is infinite, $C_v = 3R$, as in Dulong and Petit's Law. Moreover, the expression represents the doubly-inflected curves found experimentally. Thus the formula accounts very well for the results of experiment, and shows that while the atomic heat of a solid hardly varies with change of temperature at high temperatures, approximating asymptotically to the value $3R$, at low temperatures the value decreases rapidly and tends to zero. The expression was improved empirically by Nernst and Lindemann,[23] and on theoretical grounds by Debye, who considered elastic solid stationary vibrations rather than atomic oscillations.[24] These alterations did not involve any new application of the quantum theory. The experimental curves for lead, aluminium and the diamond are shown in Fig. 21.

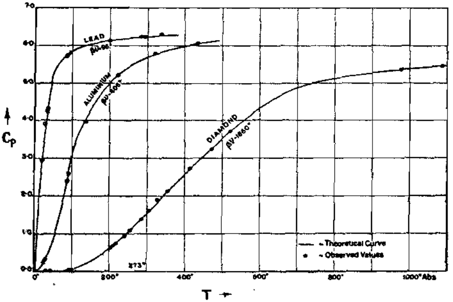
In order to test the formula, it is evidently necessary to have a method of measuring the characteristic frequency of an element. An empirical method of obtaining ν is to put into the equation an experimental value of C_v for known T, and so calculate ν, which can then be applied to other temperatures. Fortunately, however, it is possible to calculate the values of atomic frequency by independent methods. Einstein gave a relation giving ν in terms of the atomic weight of the element, its density and its compressibility.[25] It will be clear that the compressibility will affect the vibration frequency, when it is considered that the latter depends upon the restoring force tending to bring an atom into the position of equilibrium, and that this force will be greater the smaller the extensibility, or the smaller the compressibility of the substance. Again, Lindemann gave a formula connecting the melting-point of a solid with its characteristic atomic frequency, by working out the conception that melting occurs when the amplitude of vibration of the atom becomes of the same order of magnitude as the distance

between atoms.[26] At this stage, the atoms break their bonds and mingle freely with each other. In the case of lead, the compressibility is large and the melting-point is low, while the atomic weight is large. Thus vibrating lead atoms behave like heavy particles swinging attached to weak springs, and the atomic frequency is, therefore, low. These leisurely movements, the low melting-point, and the small resistance to distortion, are all connected with the low restoring force called into play when the lead atom is displaced. Since the natural

FIGURE XXI

SPECIFIC HEAT-TEMPERATURE CURVES (SOLIDS)

(See *Z. Elektrochem.*, 1911; 17, 820 *seq.*)



frequency is low, the quantum is small, according to Planck's assumption (equation (8), p. 134). Thus, even at low temperatures the available quanta may be sufficient to excite the lead atom, and the curve rises steeply as in the figure on this page. On the other hand, exactly opposite considerations are true of diamond, its melting-point being high, and its compressibility low, so that the restoring force and the frequency are large. In this case, the quantum is large, and the curve takes the form shown in the figure. (See Table VII.) Considerations based on Einstein's equation lead to the same conclusions.

TABLE VII

Comparison of Properties of Lead and Diamond

	Lead.	Diamond.
Compressibility . .	High	Low
Melting-point . .	Low	High
Atomic weight . .	High	Low
Restoring force . .	Low	High
Characteristic frequency	Low	High
Size of quantum . .	Small	Large

The quantum hypothesis has thus rendered important assistance in the interpretation of specific heats. The ideas which underlie the various calculations have been indicated. More than this introduction of the subject is impossible here. A summary of the position in regard to the extension of the quantum doctrine to solids has been given by Schrödinger.[87]

36. The Photoelectric Effect

Einstein's theory of " light-quanta " involved an extension of Planck's original conception, the radiation itself being considered to possess a quantized structure. Planck had only dealt with the absorption and emission of energy by matter, so that the classical wave theory (which explains interference and diffraction) could be retained for the propagation of radiation in space. Einstein was led to extend this conception on the basis of certain statistical calculations. It was possible to calculate the probability that the molecules of a gas are collected at a given instant in a certain fractional part of their normal volume. Einstein found that exactly the same type of formula expressed the probability that the total energy of radiation enclosed in a space should occupy the same fractional part of the volume, within the limits of Wien's radiation law. He *concluded that the radiation behaved as if built up of independent complexes of energy of magnitude $h\nu$.* Other investigations led him to the same conclusion.

The hypothesis of light-quanta is so revolutionary to those accustomed to the older wave-theory that the confirmation it has received from experiment may be examined a little further. Some of the work to which attention is drawn here is of great importance in connection with the subject of modern theories

of atomic structure. Prominent among the confirmation of Einstein's hypothesis is the work relating to the "photoelectric" effect. In 1887, Hertz observed that a spark passed more easily between metallic terminals in air when ultraviolet light (from another spark) fell on the negative terminal.[28] This discovery led to a number of investigations, notably by Hallwachs,[28] Elster and Geitel, Stoletow and Lenard. The result was attributed to the emission of rays which produced ionization in the air. The effect was a general one, and was specially noticeable with the alkali metals, and, in the case of sodium, was caused by the action of visible light. It was found that the illuminated metal lost negative charge and acquired positive charge. No satisfactory explanation of the facts was, however, forthcoming until the development of the theory of ionization of gases and the discovery of the electron. It was then found that the effect was best explained by the emission of negative electrons from the metal, which caused ionization in the surrounding gas. Thus the Hertz effect became linked with a large group of phenomena, which includes the ionization of gases by ultraviolet light or by X-rays. Lenard made extensive researches upon this and the related phenomena of phosphorescence.[29] In the latter case, according to the wave theory of light, all molecules of a phosphorescent body upon which a light wave impinges should absorb energy from the wave and all should be simultaneously capable of emitting phosphorescent light. It is actually found, however, that relatively few molecules are excited at the same time, and the wave would appear to possess a "beady" structure, having active portions where light-quanta are situated, and inactive gaps between them. Similarly, it is found that when a gas is ionized by the action of X-rays, only a small proportion of gas molecules are affected. (This was illustrated by Wilson's photographs, to which reference has been made.) Thomson called attention to these facts in 1903, before the advent of Einstein's theory of light-quanta, and attempted to explain them by supposing that the æther had a fibrous structure, so that radiant energy could travel along Faraday lines of force, conceived as localized strings in space.[30] Further, Lenard showed that the energy and, therefore, the velocity of electrons emitted by metals due to incident radiation was independent of the intensity of the light which ejected them. An increase of intensity of radiation at constant frequency caused a greater number of electrons to be emitted without affecting their velocities. Thus the velocity of an

emitted electron was dependent on the frequency of incident radiation, but not upon its intensity. Similarly, if the intensity of the light was constant, the velocities of the electrons could be changed by altering the frequency of the light. The velocity of an electron was found to increase with the frequency. According to the light-quantum hypothesis, one would expect the kinetic energy of the emitted electron to be dependent upon the size of quantum of energy received, and this, in turn, upon the frequency of the incident radiation. Increasing the intensity without altering the frequency supplies greater numbers of quanta of the same size, so that larger numbers of electrons are excited and emitted. One light-quantum $h\nu$ supplies both the kinetic energy ($\frac{1}{2}mv^2$) of one projected electron, and the energy of work done (P) in freeing the electron from its position in an atom, so that, according to Einstein's law of the photoelectric effect :—[31]

$$\frac{1}{2}mv^2 = h\nu - P \qquad . \quad . \quad . \quad (13)$$

Further, the kinetic energy of emission of the electron $\frac{1}{2}mv^2$ is equal to Ve, where e is the electronic charge and V the potential difference against which it travels before coming to rest. This law has been verified by Millikan with great accuracy for the photoelectric effect shown by the metals sodium and lithium.[32] The method actually provided a new way of estimating the value of Planck's constant, and gave $h = 6{\cdot}56 \times 10^{-27}$, in remarkable agreement with the figure derived from radiation measurements. This success of the equation would seem to go far towards supporting the theory of light-quanta. Yet this theory encounters considerable difficulty in accounting for the phenomena of interference, which were readily explained on the wave theory. It may be that the assumption of light-quanta is erroneous, but in this case some other support must be found for the above equation (13), which is so accurately in agreement with experiment. On the other hand, some explanation of interference and allied phenomena of light may be found upon the present theory of light-quanta, or upon a modification of it, and some steps have recently been taken in this direction.

The photoelectric effect may be considered as typical of a much wider group of phenomena, which includes all the cases

of impact of radiation or of electrons upon matter. Four possible cases must be noted. The impact of radiation upon matter may give rise to the emission of (1) electrons; or (2) radiation; or both simultaneously. Similarly, the impact of electrons upon matter may give rise to (3) electrons; or (4) radiation; or both together. These cases will now be considered individually.

(1) *Radiation giving rise to electrons.*—This is the general photoelectric effect, and includes the ionization of gases by X-rays, γ-rays, and ultraviolet light, as well as the emission of electrons when these rays fall upon metallic surfaces. In addition to the work already mentioned, this effect in the hands of Rutherford, Ellis, and others, has yielded results of special importance in connection with atomic structure (section 42).

(2) *Radiation giving rise to radiation.*—The scattered and characteristic secondary radiation set up when X-rays fall upon matter are examples of this group of phenomena. Further, the general effects of phosphorescence and fluorescence may be cited. According to Einstein's conception of phosphorescence, one quantum of incident radiation gives rise to one quantum of emitted light, the latter quantum being not greater than the former. Lenard supposed that excitation caused the removal of certain electrons from the molecules of phosphorescent substance, after which they became attached to certain "storage atoms," their return being responsible for the energy emitted as phosphorescent light. Similarly, the phenomenon of fluorescence has been explained on the basis of the theory of light-quanta. It has been shown that if a body is subjected to X-radiation, the frequency of which is slowly increased, the absorption suddenly increases to a high value at a certain point.[33] At the same time, the body commences to emit a secondary X-radiation in the form of a line spectrum. Thus the region of frequencies which serve to excite the characteristic K series of an element stretch from a definite point, known as the edge of the absorption band, such that the frequency of incident radiation is slightly greater than that of the "hardest" line of the series. (See section 48.)

(3) *Electrons giving rise to electrons.*—This group is represented by the ionization caused by cathode or β-rays in gases. Thus it was noted in section 22 that β-rays caused the emission of electrons from gases, though relatively few atoms became ionized by this means, and that the velocity of emission was smaller than when X-rays were employed.

(4) *Electrons giving rise to radiation.*—It will be remembered that Moseley used cathode rays to generate the characteristic X-rays of the elements. Thus the transformation of light-quanta into electronic energy would seem to be a reversible process. If the characteristic K-rays of an element are to be excited, then the kinetic energy of electrons producing them must exceed a certain critical value E_K, such that $E_K = h\nu_K$, where ν_K is the frequency corresponding to the edge of the absorption band. This has been verified by experiments conducted by Webster [34] and Wagner.[35] This work also led to a precise measurement of the constant h. Further, the cathode rays excite a "white" or continuous spectrum of rays. If a definite frequency ν of this spectrum is selected, then the light-quantum hypothesis would lead to the conclusion that a definite minimum energy E_x of an impinging electron would be necessary to excite it, such that $E_x = h\nu$. This relation has also been accurately tested by numerous investigators, and its confirmation has provided one of the most trustworthy ways of measuring Planck's constant.[36] Lastly, Franck and Hertz showed that the impact of electrons upon mercury vapour molecules excited a characteristic fluorescent line of mercury in the visible region, as long as the kinetic energy of an alectron causing the line exceeded a certain critical value E_y such that $E_y = h\nu$, where ν was the frequency of the line.[37] Further reference to this work will be made in connection with Bohr's theory of the atom.

37. Photochemistry and Reaction Mechanism

Frequent attempts have been made to test the applicability of the quantum relation to photochemical reactions. Einstein supposed that each molecule of "activated" substance contained one "resonator," and was produced by absorption of energy equal to $h\nu$, where ν was the frequency of the radiation. Thus, for a gram-molecule of substance, the energy absorbed Q may be written—

$$Q = Nh\nu \quad . \quad . \quad . \quad . \quad (14)$$

where N represents the Avogadro number.[38] This result is known as the law of photochemical equivalence. It has been deduced theoretically on thermodynamical grounds.[39] It is possible to test the relation by allowing radiation of known and suitably adjusted frequency to fall upon a reactive substance,

and by making measurements of Q_n, the energy absorbed by n molecules. The latter quantity may be measured by means of a thermopile. It often happens, however, that the primary photochemical reaction is obscured by secondary changes, and the applicability of the above law can be studied more readily, if a suitable "acceptor" is added, which can react with the molecules which have become activated by radiation. For example, Noddack finds Einstein's law to be followed in the case of chlorine activated by radiation, using trichlorobromomethane as acceptor.[40] In the absence of an acceptor, the activated molecule of chlorine gives up its energy after a very brief "life" of about 10^{-10} seconds, in the form of light or heat. Similarly, Norrish and Rideal find agreement with the law in the photochemical union of hydrogen and sulphur.[41] The absorption spectrum of S_2 vapour shows a maximum in the ultraviolet region for a wave-length of 2750 Ångström units. Applying the photoequivalence formula, inserting the value of ν corresponding to this wave-length, a value for Q is obtained of 51,670 calories per gram-atom of sulphur. This number is in exact agreement with that calculated from the temperature coefficient of the "thermal" gas reaction between hydrogen and sulphur. Ultraviolet radiation of the above wave-length was found to be active in initiating the photochemical union of the two substances. Evidence is furnished that activation may take place both by radiation and by collision, and the suggestion is made that kinetic activation may be subject to quantum dynamics, the same amount of energy being extracted from collisions, whatever the force of impact may be, as long as this force exceeds a certain critical value. The quantity of energy absorbed during activation is independent of the particular mechanism by which it is imparted, and depends only on the number of valency bonds which are broken in the process, according to views expressed by Norrish and Rideal.

The general question of the mechanism of chemical reaction is a somewhat thorny one, different views having been adopted by different authors. Perrin deduced, from an application of the law of mass action to monomolecular gas reactions, that radiation affects the mechanism of all chemical reactions. Monomolecular gas reactions conform to the law of mass action, but cannot be explained by collisions.[42] For instance, in the dissociation—

$$PH_4Cl = PH_3 + HCl,$$

the rate at which PH_4Cl breaks up per second depends at any *instant on the amount of it present in unit volume, i.e., its concentration.* This is in accordance with experimental results, by which, if the volume of reacting mixture is increased three times, the mass transformed per unit volume per second is three times smaller. A little consideration shows that the fraction of the total mass transformed in unit time is unaffected by an isothermal change in volume. It is also found to be unaltered by admixture with chemically inert gases such as argon. Now, both changes in volume and the admission of foreign gases would be expected to affect the frequency of collision, and, therefore, the "average life" of a molecule of PH_4Cl. Perrin concluded that the average life of a molecule, before its destruction by dissociation, is independent of the frequency of the collisions. By extrapolation to a vacuum, he concluded that an isolated molecule is broken up and transformed suddenly, without having undergone any collision. The agency producing this result is then postulated to be radiation. On this basis, a general theory of chemical reaction was propounded. Thus, to explain tautomeric change, as, for example, that of a molecule A into a molecule B, it was assumed that the molecule A absorbed energy Q, the combination $A + Q$ corresponding to a "critical" state. This combination could either part with energy Q and so reform molecule A, or with energy Q_1 and form molecule B. Thus $A + Q = B + Q_1$. The experiments of Wood were cited in this connection, in which it was shown that a very short interval elapsed between the absorption of energy and the emission of fluorescence in the case of mercury vapour.[43] In the above change, the heat of the change U was given by $U = Q_1 - Q$. The empirical relation of Arrhenius [44] for the dependence of reaction velocity on temperature was deduced. This had, however, already received a theoretical interpretation by Marcelin and by Rice on the basis of Maxwell's Law of the distribution of velocities among the molecules.[45] Lewis [46] and Trautz [47] had also independently announced theories of chemical reaction similar to those of Perrin. The Arrhenius relation—

$$k = s \cdot e^{-\frac{a}{RT}} \qquad . \quad . \quad . \quad . \quad (15)$$

where k is reaction velocity, T the absolute temperature, and s, a are constants has been found to be applicable to certain gas rections in another form by Dushman,[48] as follows:—

$$k = u \cdot e^{-\frac{h\nu}{TR}}$$

where ν is the frequency of absorbed radiation. Theoretical derivation of this law has also been given.[49] The exponential factor corresponds to the fraction of activated molecules.

Many criticisms have been levelled against the radiation theory of chemical change, and it is now discredited as a complete account of chemical reactivity. There is, however, no reason why the process of activation by kinetic means may not sometimes be accompanied by activation by radiation. That activation occurs is universally accepted, and this has played a part in the electronic theory of valency (section 53).

For further information, the reader is referred to a discussion of the radiation theory of chemical action held under the auspices of the Faraday Society.[50]

38. Quantum Theory and Nuclear Size

It has been observed that, in order to explain the variations of atomic heats of gases with temperature, it is necessary to postulate discontinuity of rotational energy, if the quantum theory is introduced to explain the matter. Moreover, the atomic heat of argon is constant and equal to 3 at all temperatures within wide limits, and the value for hydrogen reaches this same value within measurable distance of the absolute zero of temperature. The conclusion has been drawn that in such circumstances the energy of a gas is entirely associated with translation, so that no rotation is communicated upon impact. Thus, the minimum quantum of rotational energy is very great, and the frequency of the energy available is insufficient to provide one quantum in the case of hydrogen at low temperatures, and in that of argon at all temperatures (see p. 137). The quantum interpretation of the facts is consistent with the view that the mass of an atom is concentrated near its centre, for, if this is the case, its "moment of inertia" is small, so that it needs a larger quantum of energy to make it spin, and its minimum possible speed of rotation is very great. The argument can be put in mathematical form as follows. If ν is the frequency of revolution, corresponding to one quantum $h\nu$, and I is the moment of inertia of the atom, tnen it is shown that—

$$\nu = \frac{h}{4\pi^2 I} \quad . \quad . \quad . \quad . \quad (16)$$

where I is given, for a spherical body, by

$$I = \frac{md^2}{} \quad . \quad . \quad . \quad . \quad (17)$$

where m is the mass of the body, and d its diameter. Equation (16) shows that, when ν is large, I is small, from which it follows that d is also small, by equation (17). In the case of an atom, d corresponds with the diameter of that part where the mass is concentrated. If it is assumed that the translational energy of a molecule is less than half the quantum of rotation, it is not difficult to show that d must be less than $5 \cdot 6 \times 10^{-10}$ cm., which is considerably less than the estimated diameter of the argon molecule. The molecular kinetic energy may easily be much smaller than half the quantum of rotational energy, in which case a still smaller value of d would be obtained. In any case, the above considerations are evidently quite consistent with the conclusion already made, namely, that the mass of an atom is borne almost entirely at its centre, i.e., at the nucleus. In the above argument, however, the angular momentum for the whole atom is really considered, and the possibility of the nucleus moving in a small orbit is not excluded. The further application of the quantum theory to the question of energy levels in the nucleus of an atom and Bohr's theory of stable orbits based on the quantum conception will be considered in Chapters VII and VIII. It is, indeed, mainly on account of the latter theory of atomic structure that we have occupied ourselves with the quantum doctrine. It appears of logical importance to explain the experimental background of this conception of radiant energy before proceeding to its important relation to the subject in hand.

39. Difficulties of the Quantum Theory

It has been said that the quantum theory of energy is less an attempt to explain experimental difficulties than to focus them into one, so that if this master difficulty can be overcome, the others tend to vanish also. Properties which appear to be intrinsically different, such as the elasticity, fusibility, and specific heat of solid bodies are here linked together, and associated with one basal property, namely, a frequency characteristic of their structure. The extension to light-quanta has correlated the different cases where Einstein's photoelectric equation has been proved to be successful. But the theory, in spite of these advantages, involves many difficulties. The kinetic theory of matter was acceptable, partly because it provided a mental picture of the phenomena it undertook to explain. The quantum theory is not so adaptable in this

respect, and, moreover, its treatment is often so highly mathematical that it is sometimes difficult to appreciate the physical significance underlying a multitude of symbols. For this reason, physical conceptions have been given based on the quantum theory, the more detailed and mathematical interpretation being left to other works. At the same time, it must be admitted that the attempt can hardly be a complete success in the present state of knowledge. Let us glance at the nature of the difficulties inherent in the subject.

(1) It will be seen that considerable discrepancy appears to exist between older and newer views of the nature of radiant energy, and of the way in which it interacts with matter. Poincaré pointed out how profound would be the revolution in physics if the phenomena described do not, in fact, obey laws expressible by means of differential equations.[51] It is worthy of notice that Planck subsequently modified his theory to the extent that absorption of energy can take place continuously, retaining the idea of discontinuity of emitted energy alone. Then, in regard to light-quanta, some reconciliation is required between the older conception of a continuous electromagnetic wave and that of radiation as "done up in parcels." Moreover, the size of parcel is not always the same, depending upon the frequency of radiation. Considerable difficulty exists in making these diverse views march in step.

(2) Reference has been made to the difficulties of the newer theory in connection with interference phenomena.[52] It may be that some reconciliation will be brought about,[53] but so far only the older theory has succeeded in giving a satisfactory explanation.

(3) A further difficulty is concerned with the way in which a vibrating system can take up a whole quantum of energy when at a considerable distance from the emitting source, if it is supposed that energy-quanta are emitted at random in all directions. The chance that a vibrating atom should receive even one quantum at a considerable distance would appear to be small. In this connection, the suggestion of Thomson that the electrified particles which produce the light do not give rise to lines of force distributed uniformly in all directions but only in certain privileged directions may be helpful.[54] In any case, the vibrating systems in a source of energy will appear to be radiating evenly in all directions, if these systems are of sufficiently large number to destroy any noticeable discontinuity. Thus the physical continuity which experiment seems to require

for light-waves may be a mean effect, and not incompatible with the possibility of radiation endowed with structure.

The "quant" theory, useful as it has proved itself, does not yet possess the assured position of the atomic theory of matter. Atoms have become physical realities; we weigh them, we count them, we measure their speeds and see their tracks on a photographic plate, as in the case of α-particles, which are charged atoms of helium. On the other hand, though there is experimental evidence that the absorption and emission of radiation always takes place in quanta, the question as to whether radiation is actually propagated by discrete "light-quants" is more doubtful. Recently, however, an advance of considerable importance has been made in this connection. Compton has brought forward evidence to show that the laws of conservation of energy and of momentum hold for the impact between a light-quantum and a free electron, the characteristic monochromatic X-rays of molybdenum scattered by carbon having their wave-length increased by the predicted amount.[55] Though this result has been criticized, it has been confirmed by Becker, Watson, and Smythe, using aluminium instead of carbon to scatter the rays. This work, side by side with the progress which seems to have been made in explaining the interference difficulty, is tending to place the light-quantum on a surer basis.

In connection with the main subject of this chapter, the reader is referred to a paper by Rice,[56] and to a discussion held under the auspices of the British Association for the Advancement of Science.[57]

REFERENCES: (VI)

See Nos. 12, 20, *and* 21 *in Bibliographical List at end of book.*

1 (p. 125) H. Hertz: "Ueber die Ausbreitungsgeschwindigkeit der electrodynamischen Wirkungen"; *Wied. Ann.*, 1888; **34**, 551. *Idem*: "Ueber electro-dynamische Wellen im Luftraume, und deren Reflexion"; *Wied Ann.*, 1888; **34**, 609.
G. F. Fitzgerald: Presidential Address, Section A; *Brit. Ass. Rep.*, 1888, 557.

2 (p. 126) J. C. McLennan: "The Spectra of the Lighter Elements"; *Nature*, 1924; **113**, 217.

3 (p. 126) M. Faraday: "Experimental Researches in Electricity" (Series XI to XIV); *Phil. Trans.*, 1838; 1, 83, 125, 265. See also Series I, II, IX; *Phil. Trans.*, 1832; 125, 163: 1835, 41.

4 (p. 128) F. T. Trouton: "Repetition of Hertz's Experiments, and Determination of the Direction of Vibration of Light"; *Nature*, 1889; **39**, 391. See also *ibid.*, **40**, 398.

5 (p. 129) J. Clerk Maxwell: "A Dynamical Theory of the Electromagnetic Field"; *Phil. Trans*, 1865; **155**, 459: *Proc. Roy. Soc.*, 1864; **13**, 531.

6 (p. 130) J. J. Thomson: "The Forces between Atoms and Chemical Affinity"; *Phil. Mag.*, 1914; (vi.) **27**, 757.

7 (p. 132) S. P. Langley: "The Actinic Balance"; *Amer. J. Sci.*, 1881; (iii.) **21**, 187. See also *ibid.*, 1886; (iii.) **32**, 1, 83 and *Phil. Mag.*, 1886; (v.) **21**, 394; **22**, 149.

8 (p. 132) W. Wien: "Ueber die Energievertheilung im Emissionsspektrum eines schwarzen Körpers"; *Wied. Ann.*, 1896; **58**, 662.

9 (p. 132) Rayleigh: "Remarks upon the Law of Complete Radiation"; *Phil. Mag.*, 1900; (v.) **49**, 539.

10 (p. 134) O. Lummer and J. Pringsheim: "Die Verteilung der Energie im Spektrum des schwarzen Körpers"; *Verh. Deut. Phys. Ges.*, 1899; **1**, 23, 215.

11 (p. 134) O. Lummer and J. Pringsheim: "Uber die Strahlung des schwarzen Körpers für lange Wellen"; *Verh. Deut. Phys. Ges.*, 1900; **2**, 163.

12 (p. 134) M. Planck: "Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum"; *Verh. Deut. Phys. Ges.*, 1900; **2**, 237. See also: *Ann. Physik*, 1901; (iv.) **4**, 553.

13 (p. 135) H. Rubens and F. Kurlbaum: "Über die Emission langwelliger Wärmestrahlen durch den schwarzen Körper bei verschiedenen Temperaturen"; *Sitzungsber. P. Akad. Wiss., Berlin*, 1900; **41** 929. See also *Ann. Physik*, 1901; **4**, 649.

F. Paschen: "Ueber das Strahlungsgesetz des schwarzen Körpers"; *Ann. Physik*, 1901; (iv.) **4**, 277.

14 (p. 135) M. Planck: "Ueber das Gesetz der Energieverteilung im Normalspektrum"; *Ann. Physik*, 1901; **4**, 553.

R. Ladenburg: "Bericht über die Bestimmung von Plancks elementarem Wirkungsquantum h"; *Jahr. Rad. Elekt.*, 1920; **17**, 93.

15 (p. 136) M. Planck: "Ueber die Elementarquanta der Materie und der Elektricität"; *Ann. Physik*, 1901; **4**, 564.

16 (p. 137) M. Pier: "Die spezifischen Wärmen von Argon, Wasserdampf, Stickstoff, Wasserstoff bei sehr höhen Temperaturen"; *Z. Elektrochem.*, 1909; **15**, 537.

17 (p. 137) A. Eucken: "Die Molekularwärme des Wasserstoffs bei tiefen Temperaturen"; *Ber. Deut. Phys. Ges.*, 1912; **6**, 141.

18 (p. 138) N. Bjerrum: "Über die spezifische Wärme der Gase"; *Z. Elektrochem.*, 1911; **17**, 731: 1912; **18**, 101.

19 (p. 138) C. K. Ingold and (Miss) Usherwood: "The Specific Heats of Gases with Special Reference to Hydrogen"; *J. Chem. Soc., Trans.*, 1922; **121**, 2286.

20 (p. 138) C. Benedicks: "Über die Herleitung von Plancks Energieverteilungsgesetz aus Agglomerations-annahme; einfache Beziehung zwischen Härte und Schwingungszahl"; *Ann. Physik*, 1913; **42**, 133.

21 (p. 138) E. Grüneisen: "Das Verhältnis der thermischen Ausdehnung zur spezifischen Wärme fester Elemente"; *Verh. Deut. Phys. Ges.*, 1911; **13**, 491.

22 (p. [illegible]) A. Einstein: "Der Plancksche Theorie der Strahlung und die Theorie der specifischen Wärme"; *Ann. Physik*, 1907; (iv.) **22**, 180, 800. See also: *ibid.*, 1911; **35**, 683.

23 (p. 141) W. NERNST and F. A. LINDEMANN: "Spezifische Wärme und Quantentheorie"; *Z. Elektrochem.*, 1911; **17**, 817. See also W. NERNST: "Die Energieinhalt fester Stoffe"; *Ann. Physik*, 1911; (iv.) **36**, 395.
24 (p. 141) P. DEBYE: "Zur Theorie der spezifischen Wärmen"; *Ann. Physik*, 1912; (iv.) **39**, 789.
25 (p. 141) A. EINSTEIN: "Eine Beziehung zwischen dem elastischen Verhalten und der spezifischen Wärme bei festen Körpern mit einatomigen Molekül"; *Ann. Physik*, 1911; **34**, 170, 590. See also: *ibid.*, 1911; **35**, 679.
26 (p. 142) F. A. LINDEMANN: "Über die Berechnung molekularer Eigenfrequenzen"; *Phys. Z.*, 1910; **11**, 609.
27 (p. 143) E. SCHRÖDINGER: "Der Energieinhalt der Festkörper im Lichte der neueren Forschung"; *Phys. Z.*, 1919; **20**, 420, 450, 474.
28 (p. 144) H. HERTZ: "Ueber einen Einfluss des ultravioletten Lichtes auf die elektrische Entladung"; *Wied. Ann.*, 1887; **31**, 983.
W. HALLWACHS: "On the Electrification of Metal Plates by Irradiation with Electrical Light"; *Phil. Mag.*, 1888; (v.) **26**, 78. See also: *Wied. Ann.*, 1888; **33**, 301: 1889, **37**, 666.
29 (p. 144) P. LENARD: "Ueber die lichtelektrische Wirkung"; *Ann. Physik*, 1902; (iv.) **8**, 149.
30 (p. 144) J. J. THOMSON: Silliman Lectures, Yale, 1903.
31 (p. 145) A. EINSTEIN: "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristichen Gesichtspunkt"; *Ann. Physik*, 1905; (iv.) **17**, 132.
32 (p. 145) R. A. MILLIKAN: "A direct photoelectric Determination of Planck's *h*"; *Phys. Rev.*, 1916; (ii.) **7**, 355.
33 (p. 146) C. G. BARKLA: "Energy of Secondary Röntgen Radiation"; *Phil. Mag.*, 1904; (vi.) **7**, 543. See also: *ibid.*, 1908; **15**, 288: **16**, 550: 1909; **17**, 739.
M. DE BROGLIE: "Sur la spectroscopie des rayons secondaires emis hors des tubes à rayons de Röntgen, et les spectres d'absorption"; *Compt. Rend.*, 1914; **158**, 1493, 1785.
34 (p. 147) D. L. WEBSTER: "Experiments on the Emission Quanta of Characteristic X-Rays"; *Phys. Rev.*, 1916; **7**, 599. See also: *Proc. Nat. Acad. Sci.*, 1917; **3**, 181; 1920; **6**, 26.
35 (p. 147) E. WAGNER: "Spektraluntersuchungen an Röntgenstrahlen"; *Ann. Physik*, 1915; **46**, 868.
36 (p. 147) W. DUANE and F. L. HUNT: "On X-Ray Wave-Lengths"; *Phys. Rev.*, 1915; **6**, 166. See also: *ibid.*, 1917; **9**, 568: **10**, 624, and Ref. 34 above.
E. WAGNER: "Uber Röntgenspektroscopie"; *Phys. Z.*, 1917; **18**, 432.
37 (p. 147) J. FRANCK and G. HERTZ: "Über die Erregung der Quecksilberresonanzlinie 253, 6 $\mu\mu$ durch Elektronenstösse"; *Verh. Deut. Phys. Ges.*, 1914; **16**, 512.
38 (p. 147) A. EINSTEIN. See Ref. 31 above.
J. STARK: "Weitere Bemerkungen über die thermische und chemische Absorption im Bandenspektrum"; *Phys. Z.*, 1908; **9**, 889.
39 (p. 147) A. EINSTEIN: "Thermodynamische Begrundung des photochemischen Äquivalentgesetzes"; *Ann. Physik*, 1912; (iv.)

40 (p. 148) W. Noddack: "Neue Anwendungen des Einsteinschen photochemischen Äquivalentgesetzes"; *Z. Electrochem.*, 1921; **27**, 359. See also: P. Grüss: *ibid.*, 1923; **29**, 144.

41 (p. 148) R. G. W. Norrish and E. K. Rideal: "The Conditions of Reaction of Hydrogen with Sulphur"; *J. Chem. Soc.*, 1924; **125**, 2070.

42 (p. 148) J. Perrin: "Matière et lumière: essai de synthèse de la méchanique chimique"; *Ann. Physique*, 1919; **11**, 5.

43 (p. 149) R. W. Wood: "The Time Interval between Absorption and Emission of Light in Fluorescence"; *Proc. Roy. Soc.*, 1921; **A99**, 362.

44 (p. 149) S. Arrhenius: "Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren"; *Z. Phys. Chem.*, 1889; **4**, 226.

45 (p. 149) R. Marcelin: "Contribution à l'étude de la cinétique physicochimique"; *Ann. Physique*, 1915; **3**, 120.
W. C. M. Lewis, J. Rice, and others: Discussion on Homogeneous Catalysis; *Brit. Ass. Rep.*, 1915; 394.

46 (p. 149) W. C. M. Lewis: "Studies in Catalysis" (Parts VII, VIII, IX); *J. Chem. Soc. Trans.*, 1917; **111**, 457, 1086: 1918; **113**, 471.

47 (p. 149) M. Trautz: "Das Gesetz der thermochemischen Vorgänge (Zusammenfassung) und das der photochemischen Vorgänge"; *Z. Anorg. Chem.*, 1918; **102**, 81.

48 (p. 149) S. Dushman: "A Theory of Chemical Reactivity. Calculation of the Rates of Reactions and Equilibrium Constants"; *J. Amer. Chem. Soc.*, 1921; **43**, 397.

49 (p. 150) J. Rice: "The Velocity Constant of a Unimolecular Reaction"; *Phil. Mag.*, 1923; (vi.) **46**, 312. See also A. McKeown, W. C. M. Lewis: *ibid.*, 321, 327.

50 (p. 150) Discussion on Catalysis. Part I: "The Radiation Theory of Chemical Action"; *Trans. Farad. Soc.*, 1922; **17**, 545.

51 (p. 152) H. Poincaré: "Les rapports de la matière et de l'éther"; *J. Physique*, 1912; (v.) **2**, 347.

52 (p. 152) H. A. Lorentz: "Die Hypothese der Lichtquanten"; *Phys. Z.*, 1910; **11**, 349.

53 (p. 152) W. Duane: "The Transfer in Quanta of Radiation Momentum to Matter"; *Proc. Nat. Acad. Sci.*, 1923; **9**, 158.
A. H. Compton: "The Quantum Integral and Diffraction by a Crystal"; *Proc. Nat. Acad. Sci.*, 1923; **9**, 359.

54 (p. 152) J. J. Thomson: "On a Theory of the Structure of the Electric Field and its Application to Rontgen Radiation and to Light"; *Phil. Mag.*, 1910; (vi.) **19**, 301.

55 (p. 153) A. H. Compton: "A Quantum Theory of the Scattering of X-Rays by Light Elements"; *Phys. Rev.*, 1923; **21**, 483.
Idem: "The Spectrum of Scattered X-Rays"; *Phys. Rev.*, 1923; **22**, 409.

56 (p. 153) J. Rice: "An Elementary Account of the Quantum Theory"; *Trans. Farad. Soc.*, 1915; **11**, 1. See also R. A. Millikan: *Science*, 1913; **37**, 119.

57 (p. 153) Discussion on the Quantum Theory: *Brit. Ass. Rep.*, 1921; 473.

CHAPTER VII

ATOMIC ARCHITECTURE: (1) THE NUCLEUS

40. The Fundamental Problem

IN the foregoing pages, certain facts and theories have been presented, which will now be applied to the general question of the structures of the atoms of elements, introducing any other necessary ideas in the course of the argument. There is evidence that matter is certainly, and energy is possibly discontinuous. The unit of matter is considered here, leaving aside that of radiant energy until the available evidence in that connection shall be in a more complete state. With the structures of atoms, noteworthy progress has been made, and though the subject is still in the earlier stages of its history, the foundation which has been laid will be indicated, from which future developments may be expected.

The problem divides naturally into two parts. There is, first of all, the question of atomic nuclei, one of which is present in every atom. Considerations already advanced have shown that this nucleus, though small, may yet be extremely complex, and contain considerable numbers of protons and electrons. Although knowledge of the arrangements and movements of these parts is decidedly scanty, the present position in regard to it will be reviewed. In the second place, the spatial distribution and movements of the "planetary" electrons external to the nucleus will be examined.

Many difficulties confront the architect who designs atomic models. The proposed structures should co-ordinate optical spectra, X-ray spectra, periodic recurrence of property among elements, valency, ionization, isotopes and radioactivity. In addition, they must explain the remarkable stability of atoms. In order to accomplish this, it may be occasionally necessary to deviate from the principles of classical mechanics, but there must be some good and definite reason for so doing, and herein

lies considerable difficulty. If the result of deliberations is the production of a model which is unstable upon the basis of classical views, the problem then arises, whether the model should be abandoned, or the laws assumed to be inoperative. It has been noted that the inverse square law, for instance, does not hold within the nucleus. The natural way of attacking the problem is to hold firmly to earlier principles as far as possible, diverging from them only under the pressure of stringent necessity.

Efforts in atomic design have usually yielded models which are best adapted to explain one class of facts in particular. Thus, for instance, the atomic model associated with the names of Lewis and Langmuir was not designed to explain the phenomena of series spectra, but concentrated upon chemical relationships, valency and ionization. Bohr's theory was elaborated, on the other hand, to give an explanation of spectroscopic results, but more recently has been extended to give some account of the periodic relations of the elements. The various theories put forward in connection with the fundamental problem are discussed in the following sections.

41. Constituent Parts of Nuclei

The evidence advanced leads to the view that the simplest nucleus is that of the hydrogen atom, and that it consists of one proton, or unit of positive electricity. Passing next to the case of helium, it has been observed that the nucleus contains both protons and electrons, since, without this assumption, the mass of 4 units and charge of 2 units cannot be simultaneously accounted for (section 20). The helium nucleus, in fact, must be supposed to contain 4 protons and 2 electrons. If this view is accepted, then a somewhat striking fact is at once observed. The most accurate available value of the atomic weight of hydrogen on the oxygen scale is 1·0077, and (as no isotopes are supposed to exist) this value is taken as the mass of a neutral hydrogen atom. The mass of the electron of the hydrogen atom is about 0·0005 on the same scale, so that the mass of the proton may be taken to be 1·0072. Therefore, a neutral helium atom, which contains 4 protons and 4 electrons, should possess mass equal to $4 \times 1{\cdot}0077 = 4{\cdot}03$ units approximately. The most probable value of the mass of a helium atom, determined by density, and confirmed by the mass spectrum is 4·00. There is thus a "loss of mass" of 0·03 in building up the helium

nucleus from its elements. This discrepancy was noticed by Aston when examining the mass spectra of these substances. The difficulty has been met by assuming that, if a helium nucleus is formed from 4 hydrogen nuclei and 2 electrons, the condensation of these positive and negative charges into close proximity is accompanied by an evolution of energy. Rutherford has calculated that if a gram of helium could be built up from a gram of hydrogen, an amount of energy equal to $1{\cdot}6 \times 10^{11}$ calories would be evolved. Now, according to the "relativity" theory, a body will gain in mass when the body is moving relative to an observer. It has been observed that in the case of beta particles moving with velocities approaching that of light, this correction becomes measurable. The question arises as to whether, if it is true that a body gains mass due to an increment in its kinetic energy, it may not lose mass when energy is emitted. If this is the case, a slight diminution in mass might be expected in the formation of a helium atom from four atoms of hydrogen. The fact that this appears as an isolated instance of the effect may be due to the considerable contraction produced, with corresponding increase in stability. It is known, however, on other grounds, that the helium nucleus is a remarkably stable unit, since it is emitted from a radioactive atom without disruption, in the form of an α-particle. The α-ray must come from the nucleus of the heavy atom, and it may, therefore, be considered to be a building unit within it. This would appear, indeed, to be the simplest hypothesis, in the absence of evidence that any change occurs in the particle before and after emission. It is, therefore, regarded as a stable nuclear building unit. Aston has suggested, however, that to conclude that because a radioactive substance emits α-rays, it therefore contains them, is as unjustifiable as to conclude that a pistol contains smoke. Notwithstanding this, in the absence of other evidence, only the following three building units for nuclei will be considered: (1) the proton; (2) the electron; and (3) the helium nucleus.

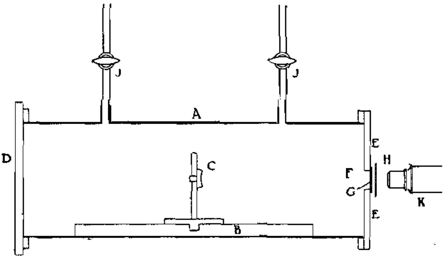
Some of Rutherford's results on the bombardment of some lighter atoms by α-particles, by which hydrogen nuclei, detected by the scintillations produced on a suitable screen, are set free, have already been noticed (see Fig. 22). It is natural to suppose that these originally formed part of the light atomic nucleus. Further, these long-range particles were observed only when dealing with atoms whose atomic weight was not an exact multiple of 4; for instance, they are not observed

with oxygen, or with carbon in the form of carbon dioxide It may be, therefore, assumed that the carbon nucleus, weighing 12 units, contains 3, and that of oxygen, weighing 16 units 4 helium nuclei. On the other hand, nitrogen, of atomic weigh

FIGURE XXII

APPARATUS FOR PASSAGE OF ALPHA RAYS THROUGH MATTER (RUTHERFORD)

(*Phil. Mag.*, 1919; (vi) 37, 543)



A. Rectangular brass box, 18 × 6 × 2 cms.
B. *Metal bar which holds support for radioactive disc C.*
D. Ground glass plate.
E. Waxed brass plate, containing small rectangular opening F, 1 cm. long × 3 mm. wide.
G. Thin plate of metal, stopping power between 4 and 6 cms. of air.
H. Zinc sulphide screen, 1 or 2 mm. from G.
J, J. *Stopcocks for admission of gas.*
K. Short focus microscope.

The whole apparatus was placed between the poles of an *electromagnet to reduce luminosity due to β-rays. In later* experiments a smaller box was used, and the source of α-rays C was arranged to slide backwards and forwards. (*Phil. Mag.*, 1921; (vi) 42, 809).

14, showed the effect, so that the presence in its nucleus of helium nuclei and 2 additional protons may be assumed. Th protons may be detached by collision with an α-particle. In al these cases, the helium nucleus of mass 4 appears as a stabl

building unit. Now, of the lighter elements studied by Rutherford, only boron, nitrogen, fluorine, sodium, aluminium and phosphorus were found to yield long-range protons.[1] Of the elements in this list, boron alone has been indicated to possess isotopes, and these have masses of 10 and 11 units respectively. In all these cases, therefore, the atomic weights will be seen to approximate to whole numbers of the form $4x + y$, where y is always either 2 or 3. It is then supposed that the appropriate value of x gives the number of helium nuclei present in the heavier nucleus, and the value of y the number of additional protons present. (Rutherford at first thought that a particle of mass 3 was emitted from nitrogen and oxygen, but has since concluded that this possibly originated in the radioactive source, and was, in reality, an ordinary particle of mass 4. The method of estimation of the mass of this particle as 3 is rendered invalid if it does not come as supposed from the medium employed. There is, therefore, at present no evidence for a new building unit of mass 3, though such a unit has been extensively employed by several authors.) It is noteworthy that beryllium, of atomic weight 9, where $y = 1$, and lithium, which consists of two isotopes of atomic weights 6 and 7, do not yield protons on bombardment. The latter case is specially remarkable, for here $y = 2$ or 3, and the effect might be expected. It is, however, possible that greater stability is inherent in the lighter atoms.

If these principles are correct, then it should be possible to estimate the number of helium nuclei in the nucleus of a heavy atom. Let us consider the case of thorium, whose atomic weight is 232, and whose atomic number is 90. Dividing 232 by 4, we get 58, the maximum possible number of helium nuclei present. Since each helium nucleus gives rise to a positive charge of two units, this number of them will correspond to $58 \times 2 = 116$ positive charges. The charge on the nucleus, however, must be equal to 90 positive units, as required by its atomic number. The presence of $116 - 90 = 26$ electrons in addition is, therefore, assumed. Now, these 26 electrons will neutralize half their number of doubly-charged particles, which is 13. There therefore remain $58 - 13 = 45$ particles unneutralized, which will equal half the atomic number. As already observed, Meitner has distinguished between neutralized and unneutralized α-particles in radioactive nuclei, and has assumed that there are two types of α-ray change, depending on whether the particle emitted was originally neutralized or

not.[2] From this, she has explained the branching in radioactive series (section 31). In the case considered above, the atomic weight was exactly divisible by 4. If, however, a remainder is left on division, then Meitner assumes, in addition to the α-particles and electrons counted by the above method, the presence of 1, 2, or 3 additional protons, according to the remainder, and a corresponding number of electrons to neutralize them. It is easily possible to express by means of symbols the general case for the numbers of the various parts of which an example has been given. This need not, however, concern us here, and may prove an exercise of some interest to the student.

A few generalizations observed in this connection will now be noted. First, except in the case of hydrogen, the atomic number of an element may be equal to, but is never greater than, half its atomic weight. Further, Harkins has observed that atoms whose atomic numbers are even are more abundant in the earth's crust than those whose atomic numbers are odd, and that the majority of such atoms have atomic weights which are exact multiples of 4.[3] This may tend to confirm ideas as to the stability of the helium nucleus as a building unit. Lastly, when the atomic weight is even, the atomic number tends also to be even, and similarly they both tend to be odd together. A little consideration will show that this means that the number of electrons in the nucleus tends to be even, and it may, therefore, be supposed that they occur in pairs.[4] Nitrogen appears to be the only known element which consists entirely of atoms whose nuclei contain an odd number of electrons. These facts are mentioned on account of their general interest, but their full significance is hardly understood at the present time.

42. Energy Levels in Radioactive Nuclei

It might be hoped that radioactive atoms, by their spontaneous disintegration, would yield some information concerning the distribution of energy within their nuclei. The velocities of the β-rays emitted by such atoms can be conveniently measured by the application of a strong magnetic field (section 4). It is possible, by this method, to produce a "spectrum of velocities," by which all particles having the same speed reach the same point on a suitably placed photographic plate. This will not present much difficulty, if the description of Thomson's method of measuring the velocity of cathode rays has been

followed, for the radius of curvature of path of an electron depends, under the influence of a given magnetic field, directly upon its velocity. It has been found by this method that the velocity spectrum of β-rays emitted by a radioactive substance shows lines as well as a continuous part.[5] The lines mean that there are groups of electrons emitted with the same velocity within each group. This is an interesting fact, and it may be reasonably connected with some regularity in nuclear structure.

It has already been mentioned (section 23) that γ-rays falling upon a metallic surface cause the emission of electrons. This has been called secondary β-radiation, to distinguish it from the ordinary β-rays emitted by a radioactive atom. It has been also found that the velocity with which the secondary β-rays are emitted depends upon the *frequency* of the incident γ-radiation. This is a particular case of the photoelectric effect (section 36). Now, Rutherford has shown that when the general γ-radiation from radium B and C is allowed to fall upon a heavy metal, the secondary radiation is emitted in groups, each having a definite velocity.[6] This fact, coupled with the nature of the line velocity spectra of ordinary β-rays, considered in the preceding paragraph, will be seen to be significant. It looks at least possible that the line spectrum of β-rays emitted by a radioactive atom may be produced by its own γ-rays. Ellis considers that this is the case, because certain lines in the ordinary β-ray velocity spectrum of radium B do, in fact, coincide with lines of the corresponding secondary β-ray spectrum.[7] The latter was produced by allowing the γ-rays from radium B to fall upon a heavy metal, and bending the secondary rays by a magnetic field in the way already described. It appears, then, that justification exists for associating the velocity line spectra of radioactive atoms with γ-rays of definite frequency.

It must next be observed that the value of the velocity of a secondary β-particle can be used to find the frequency of the γ-ray which produced it, with the aid of the quantum hypothesis. Let the frequency of the γ-radiation be ν; then, according to Planck's hypothesis, this carries quanta of energy of amounts equal to $h\nu$, where h is Planck's universal constant. Now, imagine that a heavy atom is receiving quanta of this size, and that the effect is the emission of electrons from the atom, as observed by experiment. If each quantum Q causes one electron to be emitted, then it is possible to say what will happen to this energy. Part of it P will be used as work in

causing the electron to become dislodged from the atom, and the remainder E will be retained, and will appear as kinetic energy of emission. Thus, according to Einstein's account of the photoelectric effect, $Q = P + E = h\nu$. Now, E can be calculated from the velocity v obtained from the magnetic line spectrum, for $E = \frac{1}{2}mv^2$, where m is the mass of the electron. P measures the work done in removing an electron from the atom, and will depend upon the position in the atom from which it is dislodged. It can be calculated by measurements of the "absorption edges" of X-ray spectra (section 48). From v, it is, therefore, possible to derive Q, and, since this equals $h\nu$, ν can be found. This provides a valuable method of measuring the frequency of X- and γ-rays, which can be applied when the waves are too short to be measured by reflection from a crystal.[8] In this way, by comparing the secondary β-ray velocity spectra given by different heavy metals, Ellis has measured three main frequencies of γ-rays emitted by radium B, and has accounted for six lines of the ordinary β-ray spectrum. It is supposed that each γ-ray gives rise to two secondary β-rays, depending on the level in the atom from which the electron is dislodged. Now, by converse working, from six other lines of the natural β-ray velocity spectrum from radium B, Ellis has deduced three other high frequencies as corresponding to this atom, making six in all. From these six frequencies, values of the corresponding energies (given by multiplying by h and expressing the result in volts) are obtained. These six numbers then show very simple relationships. They occur in pairs, with constant differences.

It only remains, therefore, that attention should be called to the fact that these γ-rays must come from the nucleus of radium B. In section 29 we outlined the work of Rutherford and Andrade, and gave the basis of their conclusion that the harder γ-rays measured by the crystal method arose from the nucleus. These γ-rays of Ellis, however, have higher frequency values and are harder still, as has been confirmed by their penetrating power in aluminium. It is, therefore, natural to suppose that they also originate in the nucleus. It is then possible to explain the mathematical relationships to which reference has been made, by assuming five "energy levels" in the nucleus, and by supposing that the difference in energy between two levels can be emitted. Numbering these levels 1 to 5, counting outwards from the centre, and speaking of the

energy difference between level 5 and level 4 as 5 : 4, and so on, it is evident that the difference between 5 : 2 and 5 : 1 will be the same as that between 4 : 2 and 4 : 1, or between 3 : 2 and 3·1, since each of these three differences equals that of 2 : 1. The number of combinations of five levels taking two at a time is ten, that is, there are ten different possible energy level differences. Of these, the six mentioned above correspond to Ellis's six energies of γ-rays, and the four remaining, namely, 5 : 4, 5 : 3, 4 : 3, and 2 : 1 can be shown to agree with the energy of γ-rays attributable to the nucleus, whose frequencies were measured by Rutherford and Andrade by the crystal method. This work, regarded in another way, has supplied further evidence of the validity of Einstein's equation.

It therefore appears that in radioactive atoms there are levels within nuclei, where the energy is constant at any one level, but increases outwards from the centre. This should prove important in considering the more detailed structure of the nucleus in the future. It is hoped that the account given will convey the nature of the experimental foundation upon which this conclusion is based. Amid the rival theories of radioactive change, particularly as to the origin and relationship of β- and γ-rays, it seems to be established that the hardest γ-rays arise from the nucleus, and provide some evidence as to its internal nature.

43. The Structure of Atomic Nuclei

As indicated at the beginning of this chapter, very little is definitely known with regard to the arrangement or movements of the parts within the nuclei of atoms.[9] The matter is greatly complicated by the fact that inside the nucleus the field is so intense that the ordinary generalizations of dynamics, such as the inverse square law, are not applicable. There is at present little definite experimental evidence upon which a theory may be based. The following points, however, may be noted. First, with regard to Ellis' views as to energy levels within radioactive nuclei, these levels possibly contain electrons, and the energy corresponding to a given frequency may be emitted when an electron jumps from an outer to an inner level. This argument may be capable of extension to less complicated nuclei. Secondly, Rutherford supposes that, in cases where a long-range proton is dislodged from a light nucleus by an α-particle, the proton does not form part of a helium nucleus,

but exists separately, performing possibly some kind of orbital motion near the exterior of the nuclear domain. Chwolson has conceived the nucleus to contain "petalons," or helium nuclei of disc-like shape, with electrons placed between them.[10] Somewhat similar views are advanced by Crehore, who postulates separate units of positive charge, carrying 2, 3, 4, 5 and 6 units respectively, in addition to the singly-charged hydrogen nucleus.[11] These views, however, can only be regarded as extremely tentative, though Chadwick and Bieler, following Rutherford, have concluded that the helium nucleus behaves in collision as an elastic oblate spheroid.[12] Lastly, the study of isotopes leads to the belief that more than one arrangement of the same building units should, in certain cases, be possible, and any theory which is elaborated must take this fact into account.

The problem of nuclear structure at present awaits further experimental evidence.

REFERENCES: (VII)

See No. 14 in Bibliographical List at end of book

1 (p. 161) E. RUTHERFORD: "Collision of α-Particles with Light Atoms"; (1) Hydrogen; (2) Velocity of the Hydrogen Atom; (3) Nitrogen and Oxygen Atoms; (4) Anomalous Effect in Nitrogen; *Phil. Mag.*, 1919; (vi.) **37**, 537, 562, 571, 581.

E. RUTHERFORD and J. CHADWICK: "Disintegration of Elements by α-Particles; Range of 'H' Particles"; *Nature*, 1921; **107**, 41.

Idem: "The Artificial Disintegration of Light Elements"; *Phil. Mag.*, 1921; (vi.) **42**, 809: 1922; **44**, 417: *Nature*, 1922; **109**, 584, 614. See also *J. Chem. Soc. Trans.*, 1922; **121**, 400.

2 (p. 162) L. MEITNER: "Radioaktivität und Atomkonstitution"; *Naturwiss.*, 1921; **9**, 423.

3 (p. 162) W. D. HARKINS: "The Evolution of the Elements, and the Stability of Complex Atoms"; *J. Amer. Chem. Soc.*, 1917; **39**, 856.

4 (p. 162) W. D. HARKINS: "The Constitution and Stability of Atomic Nuclei"; *Phil. Mag.*, 1921; (vi.) **42**, 305.

Idem: "The Nuclei of Atoms and the New Periodic System"; *Phys. Rev.*, 1921; (ii.) **15**, 73.

5 (p. 163) O. BAEYER and O. HAHN: "Magnetische Linienspektren von β-Strahlen"; *Phys. Z.*, 1910; **11**, 448.

Idem with L. MEITNER: "Über die β-Strahlen des aktiven Niederschlags des Thoriums"; *Phys. Z.*, 1911; **12**, 273.

J. DANYSZ: "Sur les rayons β de la famille du radium";

E. RUTHERFORD and H. ROBINSON: "The Analysis of the β-Rays from Radium B and Radium C"; *Phil. Mag.*, 1913; (vi.) **26**, 717.

6 (p. 163) E. RUTHERFORD and W. F. RAWLINSON: "Spectrum of the β-Rays Excited by the γ-Rays;" *Phil. Mag.*, 1914; (vi.) **28**, 281.

7 (p. 163) C. D. ELLIS: "The Magnetic Spectrum of the β-Rays Excited by the γ-Rays"; *Proc. Roy. Soc.*, 1921; **A99**, 261.

Idem: "β-Ray Spectra and their Meaning"; *Proc. Roy. Soc.*, 1922; **A101**, 1.

J. CHADWICK and C. D. ELLIS: "Intensity Distribution in the β-Ray Spectra of Radium B and C"; *Proc. Camb. Phil. Soc.*, 1922; **21**, 274.

C. D. ELLIS and H. W. B. SKINNER: "The Absolute Energies of the Groups in Magnetic Ray Spectra"; *Proc. Roy. Soc.*, 1924; **A105**, 60.

"A Re-investigation of the β-Ray Spectrum of Radium B and Radium C"; *Proc. Roy. Soc.*, 1924; **A105**, 165.

"The Interpretation of β-Ray Spectra"; *Proc. Roy. Soc.*, 1924; **A105**, 185.

8 (p. 164) L. MEITNER: "Über die Wellenlänge der γ-Strahlen"; *Naturwiss.*, 1922; **10**, 884.

9 (p. 165) C. G. DARWIN: "The Structure of the Atom. III. The Nucleus"; *Nature*, 1920; **106**, 116.

10 (p. 166) O. CHWOLSON: Zur Frage über die Struktur des Atomkernes"; *Z. Physik*, 1921; **7**, 268.

11 (p. 166) A. C. CREHORE: "On Atoms and Molecules"; *Phil. Mag.*, 1922; (vi.) **43**, 886.

12 (p. 166) J. CHADWICK and E. S. BIELER: "The Collisions of α-Particles with Hydrogen Nuclei"; *Phil. Mag.*, 1921; (vi.) **42**, 923.

CHAPTER VIII

ATOMIC ARCHITECTURE: (2) THE EXTRANUCLEAR ELECTRONS OF ISOLATED ATOMS

44. Levels of the Extranuclear Electrons

THE second part of the problem outlined at the commencement of the previous chapter, namely, the disposition of the electrons external to the nucleus, must now be considered. The evidence already given has led to the belief that each atom has, in its un-ionized state, a number of these equal to its atomic number.

The ideas of Thomson, put forward before the discovery of the atomic nucleus, were based on the conception that the electrons tended to arrange themselves on the surfaces of concentric spheres.[1] They were placed within a sphere of uniform positive electrification. The acceptance of the nuclear theory, however, led to the abandonment of this idea. The Rutherford nuclear atom forms the basis of Bohr's hypothesis.

It is of interest first to inquire what were the facts which led to the conception of electronic layers. It was known, from Mayer's experiments with magnets, that stable systems could be formed when the electrons were arranged in concentric rings about a centre.[2] Thomson considered the question, and showed that concentric shells containing certain definite numbers of electrons might readily form stable systems. It appears that astronomical conclusions played a part in the adoption of such an arrangement, by analogy with the rings of Saturn, and general planetary considerations. The periodic classification of the elements also indicated the same kind of result. Potassium may resemble sodium because it has a similar kind of internal structure, but, possessing more electrons, may have an additional interior sheath of them. After passing each inert gas, it might appear that the next electron begins to form another shell. W. L. Bragg's "Law of Atomic Diameters"

has significance in this connection.[3] When the diameters of the elements in Ångström units (10^{-8} cm.) are plotted against their atomic numbers, a marked periodicity is observed. (See Fig. 40, on p. 231.) Neon is assigned the value 1·30, but sodium shows a marked increase to 3·55, after which the value falls off again, until potassium is reached, where there is another sudden jump to 4·15. It certainly appears that the increase in diameter at these points is due to the formation of a new electronic layer.

The most convincing evidence, however, of ring formation comes from the study of characteristic X-ray spectra. It has been noted (section 26) that the X-ray line spectra of the element falls into well-defined groups, which have been named the K, L, M and N series respectively. These are to be attributed to the extranuclear electrons (section 30). Thus the optical spectra, shortly to be described, and these X-ray spectra are each attributed to the external electrons of atoms, as evidenced, for instance, by their similarity in the case of isotopes, where the external electrons are the same in number and probably possess an almost identical arrangement. When the frequencies corresponding to the lines of the various series of X-ray spectra mentioned above are measured, certain simple approximate numerical relationships are observed.[4] For example, the difference between the first two lines of the K series equals the frequency of the first line of the L series, and the difference between the second and the third line equals the frequency of the first line of the M series. These and other similar simple "combination" relationships between the frequencies of the lines lead directly to the conception of levels of the external electrons, known as the "K," "L" and "M" levels, and so on, in alphabetical order, by an argument similar to that used in considering the historically later work of Ellis concerning energy levels in the nucleus (section 42). Thus the K series may be explained by electrons falling into the innermost, or K level, emitting the energies corresponding to the difference between those of the levels quitted, and the K level reached.[5] For each change in energy, there will be a corresponding definite frequency. The first K line is formed by an electron passing from the L level, and the second from the M level into the K level, and so on. The L lines, similarly, are formed by electrons passing from different outer levels from the centre into the L level, and so on for the M and N series. It is found also that a certain minimum potential in the X-ray bulb is needed to excite the K series, and, when this is reached, the whole series appears

at once.[6] This is interpreted by assuming that this potential is sufficient to produce electrons of energy great enough to release an electron from the K ring, and send it outside the boundaries of the atom. In these circumstances, another electron from one of the outer rings takes its place, with emission of characteristic radiation, each line corresponding to definite energy changes in the way explained above. It is found that, the greater the atomic number of the element employed, the greater is the energy required to produce a given series. This corresponds with the fact that the binding of an electron to the nucleus increases with nuclear charge. Further, for a given atom, greater energy is needed to excite the K series than the L series, which corresponds to the fact that the K radiations are harder, and an electron in the K ring nearest to the nucleus is more strongly bound than one in another level. Lastly, it may be noted that the energy needed to send an electron from the K ring to the surface varies more in passing from one atom to that of the next higher atomic number than that required for the L ring. The wave-number of a line is fairly well represented by the following formula, due to Moseley:

$$w = R(Z - b)^2\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad (1)$$

where R is Rydberg's constant (see next section), Z is the atomic number of the element whose characteristic rays are considered, b is a constant for a given series and equals 1 for the K series, and n_1, n are whole numbers constant for a given series, the former being equal to the ordinal number (counting from the centre) of the level into which the electron falls, and the latter to the number of the level quitted.

It may be useful to compare equation (1) above with equation (6), page 107, i.e.,

$$\nu = a\,.\,(Z - b)^2 \quad . \quad . \quad . \quad (2)$$

Moseley showed that the value of a for the K series could be expressed as follows, with considerable approximation :—

$$a_K = \frac{3}{4}Rc = Rc\left(\frac{1}{1^2} - \frac{1}{2^2}\right),$$

where c is the velocity of light *in vacuo*. Similarly, a_L could be written :—

$$a_L = \frac{5}{36}Rc = Rc\left(\frac{1}{2^2} - \frac{1}{3^2}\right),$$

so that, in general,

$$a = Rc\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad (3)$$

Inserting this value of a into equation (2), and remembering that $w = \frac{1}{\lambda} = \frac{\nu}{c}$, equation (1) above follows. Rc is often written ν_0, the fundamental frequency of ordinary line spectra.

The next section shows that equation (1) resembles that which represents the wave-numbers of lines of the optical spectrum of hydrogen. This will be found to be consistent with Bohr's theory (section 46). The existence of the constant b in the equation is explained by the "screening" effect caused by certain electrons in the atom other than the one producing a line, so that the effective nuclear charge is diminished (section 27). It will be observed that equation (1) explains the "combination" relationships found, in a manner strictly analogous to that in the case of optical line spectra, which now demands attention.

45. The Nature of Optical Series Spectra

A striking difference exists between the X-ray and the optical spectra of *compounds* and those of the elements composing them. The X-ray spectra of compounds are composed of the lines of the constituent elements, whereas the optical spectra are not related in this simple way. In the case of X-rays, this result would be expected theoretically, if the characteristic lines of X-ray spectra are due to movements of electrons in the inner system of the atom, since this is presumably unaffected by combination. The behaviour of optical spectra being different, it may be supposed that their lines are due to electron movements in that part of the atom which is affected by chemical combination, namely, the region of the outer electrons. All fruitful explanations of chemical union are based upon this reasonable view.

A word may now be said as to the method by which the wave-number of a line is determined. All such measurements depend on the accurate determination of the red cadmium line by Michelson using his interferometer,[7] and also by Fabry and Perot. With this as standard, the lines of the complex iron spectrum have been determined once for all, and the frequencies

of other lines can be deduced by comparison with these. The frequency of a line can be measured with an accuracy of one part in a million. It will be remembered that the wave-number of a line is the reciprocal of its corresponding wave-length, and equals the frequency divided by the velocity of light *in vacuo*. The wave-number is, therefore, directly proportional to the frequency of a line, and is often used as a measure of it.

The optical "arc" spectrum of *hydrogen*, in a discharge tube, is by no means as simple as might be expected from the structure so far assigned to an atom of hydrogen. The spectrum consists of three different parts. First, there is a continuous spectrum, about which very little appears to be known. Secondly, there are a large number of fine lines, known as the secondary spectrum, which are attributed to the hydrogen molecule.[8] Lastly, of special importance, there are certain lines, which occur in series, the frequencies in a given series being related according to simple numerical laws. These series are associated with the names of Balmer, Lyman, Paschen and Brackett. Each consists of a number of well-defined lines, which are attributed to the hydrogen atom. The lines of a given series gradually become nearer to each other as the frequency increases towards a definite limiting value.

The simple line series in the hydrogen spectrum can be picked out by their intensity, the Balmer series, for example, being often the most marked in the visible region. Following Balmer, it has been found that the following general empirical relationship expresses the wave-numbers of the lines of the hydrogen series :—[9]

$$w = R\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad (4)$$

Here R is known as Rydberg's constant, and is the same for all series, n_1, n are simple integers, n_1 being constant for a given series. Thus, for instance, in the case of the Lyman series, $n_1 = 1$ throughout and n must be given the values 2, 3, 4 and so on, each value of n corresponding to a different line. As n increases, lines of higher wave-number, and, therefore, of frequency increasing towards a limiting value as n approaches infinity, are given by the formula. For the Balmer series, $n_1 = 2$, and n has the values 3, 4, 5, and so on. These values are tabulated below :—

TABLE VIII

Fundamental Constants of Hydrogen Series Spectra

Series.	n_1.	n.
Lyman .	1	2, 3, 4 . . .
Balmer .	2	3, 4, 5 . . .
Paschen .	3	4, 5, 6 . . .
Brackett .	4	5, 6, 7 . . .

Since classical electrodynamic theory did not explain the existence of lines, nor their simple relationships, the Bohr theory of the atom was advanced.

In the case of *singly-ionized helium*, there is, as in hydrogen, one external electron only. The series spectra of this ionized atom conform, in their general relationships, with those of hydrogen, and were at first attributed to that gas.[10] The wave-numbers of lines can be expressed in a similar fashion as the difference of two terms, which depend upon the reciprocals of the squares of whole numbers :—

$$w = 4R\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad (5)$$

Here R has almost, but not quite the same value as for hydrogen. As before, the second term will tend to vanish as n approaches infinity. The series numbers in the case of ionized helium are tabulated in Table IX.

TABLE IX

Fundamental Constants of Ionized Helium Series Spectra

Series.	n_1.	n.
Lyman .	2	3, 4, 5 . . .
Fowler .	3	4, 5, 6 . . .
Pickering .	4	5, 6, 7 . . .

When these numbers are carefully considered, it is seen that a "combination" principle applies, as in the case of the characteristic line spectra of X-rays of atoms. The combination principle of Ritz states that the wave-number of any line can be expressed as the difference between the wave-numbers of two other lines.[11] For example, it can be readily verified,

using the above formula (4), and inserting the values of n_1 and n given for hydrogen, that the wave-number of the first Balmer line is given by the difference between the wave-numbers of the first two Lyman lines, since in the subtraction the two n_1 terms cancel out.

The spectrum of *neutral helium*, where there are two external electrons, has a different character. The arc spectrum consists of two complete sets of series, both of which are extremely complicated. One is a "doublet" system, in which the lines occur in pairs, and the other a "singlet" system. It was originally thought that helium consisted of a mixture of two gases on this account, but this view has now been abandoned. It is more difficult to find a formula to fit the observed wave-numbers in this case.

Before concluding this section, a word must be said regarding the "spark" spectra of atoms. These may be produced by passing a "condensed" discharge, from a Leyden jar, through a vessel containing the substance in question. This creates a more violent disturbance than occurs in the ordinary arc discharge, where the spectrum corresponds to that obtained in a Bunsen flame. There are definite differences between the arc and spark spectra of atoms from neutral helium upwards, which have been explained by supposing that the arc spectrum corresponds to the removal of one electron from the neutral atom, and the spark spectrum of two or more. These differences do not exist in the simpler cases of hydrogen and ionized helium, where only one electron can be removed from the atom.

The more complicated arc spectra of atoms of higher atomic number from neutral helium upwards, exhibit lines which have been divided into four series, distinguished by the names principal, diffuse, sharp, and fundamental series. These also exhibit relationships, and simple relationships have been found connecting the limiting frequencies of different series. The wave-number of a line may be expressed by a formula which is similar to, though more complicated than, those given above for hydrogen and ionized helium. This formula shows the wave-number of a line as the difference between two terms, each of which depends upon the reciprocal of the square of a quantity n. But here, following Rydberg, n must be written as $n + P$ for the principal series, and $n + D$ for the diffuse series, and so on, P and D being approximately constant for the particular series under consideration.

The "multiplicity" of spectral terms of heavier atoms is not considered in this discussion.

46. The Bohr Theory of Line Spectra for one Electron

The explanation advanced by Bohr to explain the hydrogen line spectra involves the suggestion that more than one stable orbit is possible for a single moving electron, and that energy is radiated when the electron passes from one stable orbit to another nearer to the nucleus.[12] The innermost orbit corresponds with the normal state of the atom. Ionization of the hydrogen atom in the discharge tube is accompanied by the removal of the negative electron from the boundaries of the atom, and its return, according to Bohr, can occur in simple successive stages, on account of the various possible stable orbits. If it falls into any outer orbit and then passes directly into the *innermost* orbit, the Lyman series is produced, the first line by the electron jumping from the second orbit counting from the centre, the second line by jumping from the third orbit to the innermost orbit, and so on. Similarly, the Balmer series is produced by the electron passing from different outer orbits into the *second* orbit from the centre, and the Paschen series by passing into the *third* orbit. Each orbit has a definite corresponding amount of energy, and the frequency, and, therefore, the wave-number of a line produced depends upon the *difference in energy between that of the orbit left and that of the orbit reached* by the electron. Thus, an electron in returning towards the nucleus can pass from one orbit to the next, or it can skip intermediate stages. At any given instant, in the mass of atoms, all kinds of different changes are simultaneously realized by different atoms. Thus all the lines are observed together. (See Fig. 23.)

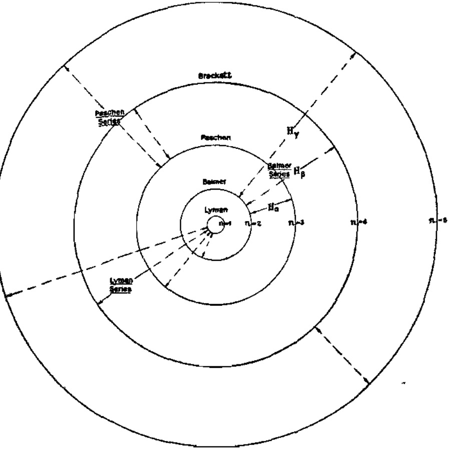
On the basis of the assumption of more than one stable orbit for a single electron, it is possible to account for the combination principle of Ritz. The wave-number of the first Balmer line produced by an electron passing from the third orbit to the second orbit will be equal to the difference between the wave-numbers of the first two Lyman lines produced by the electron falling from the second and third orbits respectively into the first, and so on in other cases. This is because the wave-number of a line depends directly, according to this theory, upon the difference between the fixed energies corresponding to two different orbits. The wave-number of the first Lyman line is greater than that of the first Balmer line, so that, according to the theory, there will be a greater energy difference between the innermost orbit and the second than between the

second and the third. It may, therefore, be concluded that the energy differences between consecutive orbits decrease outwards from the innermost orbit, though the theory demands,

FIGURE XXIII

CIRCULAR ORBITS IN HYDROGEN (BOHR)

(*Nature*, 1923; **112**, 34)



In order to account for the observed series line spectra of hydrogen, Bohr postulated a number of stable stationary orbits for the negative electron of the hydrogen atom, the orbits being fixed by a "quantum" condition. No energy is radiated by the atom so long as the electron remains in a given orbit, but energy of definite frequency is emitted when the electron passes from one stable orbit to another nearer to the nucleus (at the centre of the circles shown above). In this way, Bohr successfully calculated the frequencies of the lines observed (see text).

since energy is *emitted* when an electron passes from an outer to an inner orbit, that the energies of the orbits shall increase from orbit to orbit from the centre outwards. A little consideration will show that the energies of the orbits increase towards a definite limiting value. In these circumstances, the lines of a given series will steadily increase in frequency towards a limiting value, as has already been observed to be the case. Bohr, however, has given much more than a qualitative explanation of the above kind. By departing to some extent from classical electrodynamics, he has attempted to account for the stability of the orbits which have been postulated, and he has derived, upon certain postulates, an expression for the wave-numbers of the lines observed.

It is now important to examine the nature of these orbits more closely, and especially the meaning to be attached to the phrase "energy of an orbit." It may first be noted that these orbits differ from the K, L and M levels used in the explanation of characteristic X-ray spectra, in that they are frequently unoccupied, whereas the latter levels are presumed to contain electrons in their normal condition. Next, the energy of an electron of a hydrogen atom in a given orbit will be expected to be constant at all points in the orbit, and independent of the position of the electron, because a nucleus and a single electron comprise a "self-contained system." The energy of the system as a whole, however, is not exactly equal to that of the electron alone, for the following reason. Considering the force of attraction between the hydrogen nucleus and its electron (which force holds the electron in its path), the action is evidently reciprocated by the electron on the nucleus. If the nucleus were so heavy that the electron could not appreciably displace it, it could be treated as fixed, but it has been shown that in the case of hydrogen its relative mass (compared with the electron) approximates to 2000. In these circumstances, the attractive influence of the electron on the nucleus must be imagined to produce a slight displacement, so that the centre of mass (the point about which both the nucleus and electron rotate) is not at the nucleus, but at a near position determined by the ratio of the masses of the two particles. It is, therefore, possible to treat the system as one in which the nucleus is of comparatively large mass, and, therefore, fixed, by assigning a suitable "effective" mass to the electron. If three points N, G and E, in this order in a straight line, are such that N and E represent the respective positions of the nucleus and the electron, and G that

of the centre of mass which is very near to N, and if M, m are the masses of the nucleus and the electron respectively, then NG : GE = $m : M$. If the effective mass of the electron about G involves a decrease in m in the ratio GE : EN, which is GE : (GE + GN), or $M : (M + m)$, then the mass of the nucleus may be treated as if infinite, by substituting for m in the expressions reached the value $mM/(M + m)$.

The next point which arises is the meaning of the energy of the system, in the case of the hydrogen atom with the electron executing a given orbit, treating this energy as equal to that of the electron alone. The electron has potential as well as kinetic energy, and its total energy is the sum of these two. Potential energy is always measured relative to some standard configuration; thus it is referred in the case of a body to the level of the ground or to sea level, and equated to the work done in raising it from some such fixed lower level to the position occupied. In the case of the atom, the potential energy of the electron is taken to be zero when removed from the sphere of influence of the nucleus. Its capacity of doing work, however, is greatest when it is free from the binding force of the nucleus, and it loses potential energy as it falls in towards the nucleus. Hence, when it is executing an orbit, its potential energy is less than at the boundary of the atom, and is, therefore, taken as negative. The kinetic energy is greatest in the innermost orbit, and has a positive sign. Thus the algebraic sum, that is, the arithmetical difference, of the two energies measures the energy in a given orbit. Following this convention, a negative value for the energy E in an orbit would be obtained. It is, therefore, convenient, in order to deal with a positive quantity, to speak of the "negatived" total energy W, which will be equal (numerically) to the absolute value of the potential energy less that of the kinetic energy associated with the orbit. This will be examined further in the mathematical argument below.

Certain results of mechanics are required in this connection. In the first place, an electron executing a given orbit moves under the influence of a force which is directed towards a point, namely, the position of the nucleus, here assumed to be fixed. In classical mechanics, expressions are given, in the case of a body moving in a plane according to any law, for the resolved parts of its velocity and its acceleration along the line joining it at any instant to a fixed point (taken as origin), and also along a direction perpendicular to this "radius vector," in

erms of its "polar co-ordinates" r and θ. The former co-ırdinate measures the radius vector, and the latter the angle he radius vector makes with a fixed direction. If v_1, v_2 are he velocities resolved along and perpendicular to the radius 'ector respectively, and f_1, f_2 are the corresponding accelerations,

$$v_1 = \dot{r} \quad . \quad . \quad . \quad . \quad (6)$$
$$v_2 = r\dot{\theta} \quad . \quad . \quad . \quad . \quad (7)$$
$$f_1 = \ddot{r} - r\dot{\theta}^2 \quad . \quad . \quad . \quad . \quad (8)$$
$$f_2 = r\ddot{\theta} - 2\dot{r}\dot{\theta} \quad . \quad . \quad . \quad . \quad (9)$$

vhere $\dot{r}$ denotes the differential coefficient of r with respect to ime, and $\ddot{r}$ the second differential coefficient, and similarly for . Thus, equation (6) means that the velocity along the radius ector is measured by the rate of change of its length with time, nd equation (7) that the velocity perpendicular to the radius ector is measured by r times the rate of change of the angle θ /ith time, or by r times the "angular velocity."

Now if the force acting on the body is directed to the fixed oint, as in the case of an electron moving under a force directed owards the nucleus of an atom, the force, and, therefore, the cceleration at right angles to the radius vector is zero. If the alue of f_2 as given by equation (9) above is equated to zero, : can be easily shown that equal areas are swept out by the adius vector in equal times, and that the "angular momentum" s constant at all points in the path. The angular momentum s the mass of the electron multiplied by the velocity at right ngles to the radius vector and the radial distance r. It is also alled "moment of momentum," which name may assist the eader to understand the definition. It is, therefore, equal to $mv_2 . r$, or, using equation (7), to $mr\dot{\theta} . r = mr^2\omega$, where $\dot{\theta} = \omega$ he angular velocity.

Further, if it is assumed with Bohr that an inverse square aw of force holds, so that the force between the electron and he nucleus is inversely proportional to r^2, then it is known hat the path traced out is a conic, one of whose foci lies at the xed nucleus. Therefore, if an electron executes a *closed* path nder this law of force, the path is an ellipse having the nucleus t one focus, or, in the limiting case, a circle, with the nucleus t the centre.

The fundamental assumptions made by Bohr for an atom aving a single electron will now be given, noting in what espects they deviate from classical electromagnetic theory. he arrangement of the following five postulates is our own.

Postulate 1.—The electron moves in a closed path under the influence of an attraction directed towards the nucleus. The force of attraction varies inversely as the square of the distance between the electron and the nucleus. (By classical mechanics, the path of the electron is either an ellipse or a circle. In this section, circular orbits only will be considered.)

Postulate 2.—The electron can circulate with an acceleration directed towards the nucleus without radiating energy. [This is in contradiction to classical theory, by which every acceleration of an electron involves the emission of energy (section 33). According to the older theory, radiation would be emitted, accompanied by movement of the electron towards the nucleus, and ultimate absorption in it.]

Postulate 3.—More than one stable orbit is possible for the electron. These comprise its "stationary" orbits, each orbit being associated with a definite amount of energy.

Postulate 4.—The possible number of stationary orbits is limited by the condition that tbe angular momentum (or moment of momentum) increases by equal amounts in passing from one orbit to the next. Stationary orbits are only possible for which the angular momentum multiplied by 2π (for one revolution) is equal to nh, where n is a whole number, and h is Planck's universal constant. The angular momentum is thus "quantized." The value of n defines the orbit, and n is its "quantum number." For the innermost orbit, $n = 1$; for the next $n = 2$, and so on.

Postulate 5.—Energy of definite frequency is radiated when the electron jumps from one stable orbit to another nearer to the nucleus. The amount of energy emitted ϵ is determined by the difference between the energies of the two stable orbits. The frequency of radiation ν corresponds with this amount of energy divided by h, Planck's constant of action, so that we may write—

$$\epsilon = E_{n_1} - E_n = h\nu \quad . \quad . \quad . \quad (10)$$

where E_{n_1}, E_n are the energies of the orbits concerned. Actually, the energy of revolution in the inner orbit is the greater; in what way this may be regarded as consistent with the *emission* of energy will be shortly explained. The wave-number w of frequency ν is given by ν/c, so that we have—

$$w = \frac{E}{hc} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

n harmony with equations (1) and (2) of the previous chapter.

The postulates mark deviations from classical theories. First, a contradiction has been noted under postulate 2. In this connection, however, the remarks of Livens and of Schott are of interest.[18] Secondly, the quantizing of angular momentum (postulate 4) is a new departure. No reason exists, apart from the quantum theory, why orbits should not exist for all possible angular momenta. Lastly, the application of the quantum theory and the introduction of Planck's constant into postulate 5 is a new assumption. Upon classical theory, the frequency of emitted radiation would be expected to be equal to the orbital frequency of revolution, the conception here introduced being quite different. The usefulness of the quantum theory has already been outlined, and it enters into Bohr's theory of orbits, not only to provide stable orbits, but also to account for the line spectra of an atom or ion having one external electron.

Bohr's expression for the wave-numbers of line spectra will now be deduced, assuming for the present that the electron executes circular orbits only. This assumption will be found to be sufficient, on the basis of the postulates, to account for the empirical formulæ already given. The present considerations will apply to the case of one external electron moving round a nucleus, and will include hydrogen and singly-ionized helium, as well as doubly-ionized lithium. In the case of lithium, however, experimental confirmation is so far incomplete. Let Ze, e and M, m be the charges and masses of the nucleus and the electron respectively, where Z is the atomic number of the atom. Let v, ω be the linear and angular velocities of the electron, which moves in a stable orbit of radius r. The nucleus will be taken to be at rest, and in using m as the mass of the electron, more exact expressions will be obtained by substituting for m the value $mM/(m + M)$, by the argument previously given, in which the finite mass of the nucleus is taken into account. Consider now the potential energy of the electron in an orbit. This is measured by the work done in bringing the electron from a position *at rest* in an orbit to infinity, i.e., to a position outside the influence of the nuclear attraction. If the electron is moved through an infinitesimal distance dr against the attractive force Ze^2/r^2 (given by the inverse square law), the work done is Ze^2/r^2dr. If we now integrate with respect to r, the potential energy $J = -Ze^2/r$ plus an integration constant. If J is zero when r is infinite, according to considerations on

page 178, the constant of integration is also zero. Thus it follows that—

$$J = -\frac{Ze^2}{r} \quad . \quad . \quad . \quad . \quad (12)$$

where the negative sign indicates that this work must be done on the electron to remove it to infinity. In this way, the potential energy of the electron in an orbit may be regarded, as Lodge has pointed out, rather as a debt than an actual possession. Further, the kinetic energy of the electron is given by the familiar expression $\frac{1}{2}mv^2$, where v is its velocity. This can be expressed in terms of the charges concerned as follows. By equating the expression for "centrifugal" force mv^2/r to the force of attraction given by the inverse square law,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2},$$

or,

$$\frac{1}{2}mv^2 = \frac{Ze^2}{2r} \quad . \quad . \quad . \quad . \quad (13)$$

which is just half the absolute value of the potential energy given by equation (12) above. Moreover, it is greatest when r is least, so that the smallest orbit possesses the greatest kinetic energy. Next suppose that the electron moves from an outer orbit of radius r_2 to an inner orbit of radius r_1. The work done by the attractive force is equal to—

$$+ Ze^2\left(\frac{1}{r_1} - \frac{1}{r_2}\right),$$

according to equation (12) above. This work done provides the increase in kinetic energy of the inner orbit, equal to—

$$\frac{Ze^2}{2}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

by equation (13). Thus the increase in kinetic energy is one-half of the work done, and a surplus of energy remains for radiation. It comes about in this way that there is an emission of energy, in spite of the fact that the kinetic energy is increased in moving from an outer orbit to an inner orbit. From what has been said, the electron, in passing from an outer to an inner orbit, gains kinetic energy and loses potential energy, similarly to a body falling under gravity. In the case of the

lectron, the force is not constant, and if the inverse square aw holds good, the energy equivalent to the potential energy ost in passing from an outer orbit to an inner is twice as great s the additional kinetic energy necessary for circular motion n the new orbit. The balance appears as radiation of definite requency, according to equation (10) on page 180. The total nergy in an orbit is given by—

$$E = \frac{1}{2}mv^2 + J$$
$$= \frac{Ze^2}{2r} - \frac{Ze^2}{r},$$

ccording to equations (12) and (13) above, so that—

$$E = -\frac{Ze^2}{2r} \quad . \quad . \quad . \quad . \quad (14)$$

Iere the negative sign denotes that this amount of energy must e supplied to remove the electron to infinity. The energy eeded to expel an electron from an orbit is equal to its own inetic energy. Now, let $W = -E$, so that W is positive, nd expresses the "negatived" total energy. Thus—

$$W = \frac{Ze^2}{2r} \quad . \quad . \quad . \quad . \quad (15)$$

o that W varies inversely as the diameter of the orbit for a iven nucleus.

The quantizing condition mentioned in postulate 4 must ow be introduced, by which the moment of momentum, or ngular momentum (which measures the rate of sweeping out qual areas) is given by—

$$m\omega r^2 = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad (16)$$

here ω is the angular velocity, given by

$$\omega = \frac{v}{r} = 2\pi N \quad . \quad . \quad . \quad (17)$$

here N is the frequency of revolution. Now from equations 13), (16), and (17), v and ω can be eliminated, whereby

$$r = \frac{h^2}{4\pi^2 e^2 m} \cdot \frac{n^2}{Z} \quad . \quad . \quad . \quad (18)$$

where n is the quantum number of the orbit. In this way, the radii of successive orbits increase as the squares of whole numbers for a given value of Z. As Z increases, the radii of corresponding orbits diminish in inverse proportion. Thus, the radius of the innermost orbit in ionized helium is half that of the same orbit in hydrogen. If this value of r is substituted into equation (15),

$$W = \left(\frac{2\pi^2me^4}{h^2}\right)\frac{Z^2}{n^2} = q\frac{Z^2}{n^2}. \quad . \quad . \quad (19)$$

where q is the constant portion within the bracket, equal to $2\pi^2me^4/h^2$, or, more exactly, when the finite mass of the nucleus is taken into account by substituting $mM/(m + M)$ for m,

$$q = \frac{2\pi^2mMe^4}{h^2(m + M)} \quad . \quad . \quad . \quad (20)$$

Now, equation (19) shows that W varies inversely as n^2 for a given atom, and thus decreases rapidly as we pass from orbit o orbit outwards from the centre. For the same orbit (e.g. he innermost) of two atoms, W varies as Z^2, and thus increases apidly as Z is increased. Returning now to postulate 5, and o equations (10) and (11), the energy ϵ emitted when an electron umps from an outer orbit of quantum number n to an inner rbit of quantum number n_1 is given by—

$$\epsilon = W_{n_1} - W_n$$
$$= \left(\frac{1}{n_1^2} - \frac{1}{n^2}\right)qZ^2$$

that, by equation (11), page 180, the wave-number w is given y—

$$w = \left(\frac{1}{n_1^2} - \frac{1}{n^2}\right)\frac{qZ^2}{hc} \quad . \quad . \quad . \quad (21)$$

hich has exactly the form of the empirical equations (4) and (5) this chapter, if the constant R is identified with the constant rt outside the bracket, i.e., if

$$R = \frac{q}{hc} \quad . \quad . \quad . \quad . \quad (22)$$

us, in the case of hydrogen, $Z = 1$, and equation (21) reduces equation (4) on page 172. For ionized helium, $Z = 2$, so

that $Z^2 = 4$, and we reach equation (5) on page 173. Further, if the value of q given by (20) is inserted in (22),

$$R = \frac{2\pi^2 m M e^4}{h^3 c(m + M)} \quad . \quad . \quad . \quad (23)$$

It has been already observed that the value of R is not exactly the same for hydrogen as for ionized helium, and the reason for this will now be clear, since (23) involves the mass of the nucleus M. By means of this equation, R can be evaluated for the two cases, since all the quantities in the expression above are known from other work. It is, therefore, possible to verify, by evaluating the constants concerned, that R (which has the dimensions of w, i.e., the reciprocal of a length) approximates closely to the experimental values, namely, 109,768 for hydrogen, and 109,722 for ionized helium, the unit of length being the centimetre, of mass the gram and of charge the electrostatic unit. This remarkable agreement in the value of R shows that equation (21) correctly expresses the wave-numbers of the lines of the series spectra in the two cases. The applicability of the above equation (23) can be tested in other ways. For example, by applying it first to hydrogen and then to ionized helium, the ratio of the experimentally determined values of R can be expressed in terms of the masses of the two nuclei and that of the electron. All the quantities in the expressions for R_H and R_{He} cancel out when the ratio is taken, except those of the masses. Remembering that the mass of the helium nucleus is almost exactly four times that of hydrogen, a ratio for the mass of an electron to that of the hydrogen nucleus is obtained in harmony with the value obtained by other methods. Lastly, from this, a value of the ratio of the charge to mass of an electron can be derived, in agreement with the most reliable work. It is also of special interest that Moseley's results on the X-ray spectra of heavier atoms are in harmony, as inspection of equation (1) on page 170 will show. In these cases, however, large numbers of external electrons are concerned, so that the constant b accounts for the screened nucleus. Thus, from several points of view Bohr's theory is capable of giving an account of the facts, and it can hardly be doubted that his conception has some correspondence with what actually occurs when monochromatic radiation is emitted.

47. Absolute Magnitudes relating to Circular Orbits

The formulæ deduced in the previous section enable calcula tions to be made which yield values of various magnitude relating to circular orbits. These formulæ are strictly appli cable only to hydrogen and ionized helium. It is certain tha the simple equation (13) on page 182 does not hold for the oute electrons of more complicated atoms. Moseley's results, how ever, would seem to indicate that relations of similar type hold good for the inner orbits of atoms of higher atomic number. Thus, some justification may be offered for making extensions to heavier atoms, in an approximate kind of way, as carried out below. The following attributes of the orbits will be considered, with special reference to the K orbit of hydrogen: (1) radius, (2) velocity, (3) angular momentum, (4) kinetic energy and (5) ionization frequency.

(1) *Orbital Radius.*—According to equation (18) on page 183, we have—

$$r = \frac{h^2}{4\pi^2 e^2 m} \cdot \frac{n^2}{Z}$$

where n is the quantum number of the orbit, which is the same as the ordinal number of the orbit counting from the centre of the atom. It is observed that r varies as n^2/Z. Thus, within the limits of applicability of the above expression, if r_K, r_L, r_M are the radii of successive orbits from the centre, for a given atom,

$$r_K : r_L : r_M \ldots = 1 : 4 : 9 \ldots$$

By inserting the values of the constants in the expression, r_K for hydrogen is 0·532 A.U., which is about the size attributed to the normal hydrogen atom. Further, it may be deduced that as Z is increased, the radii of orbits of the same quantum number decrease in inverse proportion. The radius of the K orbit of uranium is about 1/92nd of that of the K orbit in hydrogen.

(2) *Orbital Velocity.*—From equations (13), (16), and (17) of the preceding section, it follows that—

$$v = \frac{2\pi e^2}{h} \cdot \frac{Z}{n} \quad . \quad . \quad . \quad (24)$$

here v varies as Z/n. Thus, for a given atom,

$$v_K : v_L : v_M \ldots = 1 : \frac{1}{2} : \frac{1}{3} \ldots$$

and the velocities in corresponding orbits in different atoms will vary directly as Z. The speed of the electron in the K orbit in hydrogen, according to the above expression, is $2{\cdot}2 \times 10^8$ cms. per second, or about 1300 miles a second. It is clear that the velocities of inner orbits of the higher elements will be near to the velocity of light, where a correction for change of mass must be introduced, as in the case of the beta rays already considered. Thus mass increases with velocity very rapidly as the velocity of light is approached, tending towards infinity. It does not seem inherently improbable that the kinetic energies of electrons and α-particles in the neighbourhood of a very heavy nucleus are so enormous that radioactive disingteration results.

On the other hand, the angular velocity ω, with which the frequency of revolution in an orbit is simply related according to equation (17), varies in a different manner. Since $\omega = v/r$, inserting the values of v and r given by the expressions given above,

$$\omega = \frac{8\pi^3 e^4 m}{h^3} \cdot \frac{Z^2}{n^3} \quad . \quad . \quad . \quad (25)$$

Thus ω varies as Z^2/n^3, and the angular velocities of orbits of a given atom will vary according to the following :—

$$\omega_K : \omega_L : \omega_M \ldots = 1 : \frac{1}{8} : \frac{1}{27} \ldots$$

The angular velocities of orbits of the same quantum number will vary as Z^2. The frequency of revolution N, which is $\omega/2\pi$, may be evaluated for the hydrogen K orbit as $6{\cdot}6 \times 10^{15}$ revolutions per second. It will be found, taking R as equal to $2\pi^2 me^4/h^3 c$, that—

$$N = 2Rc\frac{Z^2}{n^3} \quad . \quad . \quad . \quad . \quad (26)$$

Moreover, the periodic time t equals $1/N$, so that for a given atom, t varies as n^3 while r varies as n^2, from which it follows that t^2 is proportional to r^3.

(3) *Orbital Angular Momentum.*—This equals mvr, or $nh/2\pi$, which is independent of Z. As already pointed out, the angular momentum is a measure of the rate at which the radius vector sweeps through equal areas. This rate for the K orbit is the

unit of angular momentum $A = h/2\pi$, or $1{\cdot}04 \times 10^{-27}$ C.G.S. units. For a given atom, according to the quantizing principle,

$$A_K : A_L : A_M \ldots = 1 : 2 : 3 \ldots$$

(4) *Orbital Kinetic Energy.*—This is $mv^2/2$, and is given in terms of constants by using the value of v of equation (24). It will be found that the kinetic energy T is given by—

$$T = Rch\frac{Z^2}{n^2} \quad . \quad . \quad . \quad . \quad (27)$$

the connection between T and the frequency of revolution N being, by equation (26),

$$T = \frac{1}{2}nhN \quad . \quad . \quad . \quad . \quad (28)$$

This equation is analogous to that of Planck $E = n(h\nu)$ (where n is a whole number), and formed the basis of Bohr's original ssumption. It may be readily converted into equation (16) n page 183, involving angular momentum, based on the ourth postulate, by eliminating T and N, using the relations $= \frac{1}{2}mv^2 = \frac{1}{2}m(r\omega)^2$ and $N = \omega/2\pi$. Therefore, for a given tom,

$$T_K : T_L : T_M \ldots = 1 : \frac{1}{4} : \frac{1}{9} \ldots$$

he value of T for the K orbit of hydrogen may be evaluated $2{\cdot}15 \times 10^{-11}$ ergs. This amount of energy must be supplied enable the electron to escape, i.e. to ionize the atom. Thus, " ionization potential " V equal to T/e must be supplied, ice V refers to unit charge, so that—

$$V = \frac{2{\cdot}15 \times 10^{-11}}{4{\cdot}77 \times 10^{-10}} \times 300$$
$$= 13{\cdot}5 \text{ volts.}$$

(5) *Orbital Ionization Frequency.*—The frequency of radian necessary to expel an electron from a given orbit in an m will be the same as the frequency emitted when an electron s from infinity into the orbit. The latter is given by the eral formula—

$$\nu = Rc\frac{Z^2}{n_1^2} \quad . \quad . \quad . \quad . \quad (29)$$

where n_1 is the quantum number of the orbit. This follows from equation (21) on page 184, since $\nu = cw$ and $R = q/hc$, since the second term vanishes when the quantum number becomes infinite. For the K orbit of hydrogen, the above expression reduces to Rc, which is $3{\cdot}3 \times 10^{15}$ per second, or half the frequency of revolution in the K orbit. The quantity Rc is the fundamental frequency of line spectra. It is sometimes known as the Rydberg Number, and equals what has been termed the Rydberg Constant (based on wave-number) multiplied by the velocity of light. The wave-length corresponding to this frequency is 914 A.U. The ionization frequency of the K orbit of another atom is given according to the above expression by multiplying Rc by Z^2. The leading results obtained are collected in Table X.

TABLE X

Innermost Orbital Data (Hydrogen) and Related Constants

Planck's fundamental constant h	$6{\cdot}547 \times 10^{-27}$ C.G.S. units
Unit of angular momentum $A = h/2\pi$	$1{\cdot}04 \times 10^{-27}$ C.G.S. units
Rydberg wave-number constant R (hydrogen)	109,768 per cm.
Rydberg frequency constant Rc	$3{\cdot}3 \times 10^{15}$ per sec.
Radius of K orbit (hydrogen)	$0{\cdot}532 \times 10^{-8}$ cm.
Velocity in K orbit (hydrogen)	$2{\cdot}2 \times 10^{8}$ cms. per sec.
Frequency of revolution in K orbit (H)	$6{\cdot}6 \times 10^{15}$ per sec.
Kinetic energy of K orbit (hydrogen)	$2{\cdot}15 \times 10^{-11}$ ergs.
Ionization potential [K orbit (H)]	$13{\cdot}5$ volts
Ionization frequency [K orbit (H)]	$3{\cdot}3 \times 10^{15}$ per sec.
Wave-length corresponding to this frequency	914 A.U.

Other fundamental constants will be found in Table II on page 38.

48. Elliptic Orbits

It has been stated that the path traced out by a particle moving under a force directed to a fixed point which varies inversely as the square of the distance is a conic, according to classical mechanics. If the orbit is closed, it will be either a circle or an ellipse. In a circular path, the point to which the acceleration is directed is at the centre, while in an elliptical path it is at one focus. It has been seen that the assumption of a circular path is capable of leading to many results in agreement with experiment. Further evidence has, however, indicated that this assumption is insufficient to explain all observed phenomena.[14] In 1915, Sommerfeld developed the theory of elliptic orbits, and applied it to an explanation of the "fine

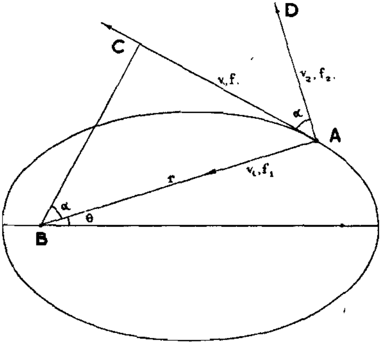
structure" of the hydrogen lines. This is revealed by using a spectroscope of high resolving power, when the lines are found to consist of components with very small frequency differences. This suggests that electrons of a given "energy level" may not possess exactly the same amounts of energy. The treatment suggested by Sommerfeld has played an important part in the development of the theory of elliptic orbits, for circular orbits alone offer no explanation. The case of the elliptic orbit will now be treated, without mathematical analysis.

Let an electron execute an elliptical orbit under an inverse square law of force directed towards the nucleus at one focus. Let the position of the electron be defined by means of its "polar co-ordinates," referred to the nucleus as origin, and the major axis as fixed direction, as in Fig. 24. Then, in order to define the position of the electron at any instant, the length of the radius vector r, and its direction, given by the angle θ which it makes with the major axis, must be stated. In the case of the circular path, the direction of movement is always at right angles to the radius vector, so that the velocity of the electron has no component along it. The acceleration, directed along the radius vector, has no component in the direction of movement, and, therefore, the particle moves with constant speed. With the ellipse, however, it is different. The radius vector varies, not only in direction but also in length, and the direction of movement (except when the electron is at either end of the major axis) is not perpendicular to it. The acceleration of the particle has, in general, a resolved component in the direction of movement, i.e., along the tangent at any point, and, therefore, the particle does not move with constant velocity. The angular momentum, however, is still constant at all points in an orbit, as already indicated for the general case where movement takes place under any force directed to a point. The velocity of the electron at any point in its path may be resolved into radial and transverse components in directions respectively along and perpendicular to the radius vector. The transverse component of velocity multiplied by the mass of the electron and the radial distance gives the moment of momentum, or angular momentum of the electron. If this is now quantized as in the case of circular orbits, a relation is obtained which is insufficient to define the elliptic path. The reason for this is that the angular momentum depends on the transverse component of velocity, so that the radial component is not taken into account. The radial component of velocity

corresponds with "radial momentum," which, however, varies continuously in an orbit. The radial momentum over one complete revolution is quantized. In this way, a second quantum condition is obtained, and the ellipse is then defined. This leads to the two quantum conditions set forth below.

FIGURE XXIV

ELECTRON IN ELLIPTIC ORBIT



A represents an electron of mass m moving with velocity v and acceleration f in an elliptical path under a force acting along the radius vector A B, where B is a focus of the ellipse and is the position of the positively charged nucleus. The velocities and accelerations of the electron along and perpendicular to the radius vector are v_1, f_1 and v_2, f_2 respectively. The angular momentum (or "moment of momentum") is measured by $mv \times$ BC, which equals $mvr \cos \alpha$, and is constant. Because no force acts along AD, $f_2 = 0$, and it follows that the radius vector sweeps through equal areas in equal times (*see* standard text-books on mechanics).

(1) The constant angular momentum of an orbit (multiplied by 2π for one revolution) is put equal to kh, where k is a whole number, known as the "azimuthal" quantum number, thus:

$$mr^2\omega = \frac{kh}{2\pi} \quad . \quad . \quad . \quad . \quad (30)$$

(2) The variable radial momentum (for one revolution, obtained by integrating it with respect to r within the limits $\theta = 0$ and $\theta = 2\pi$, as expressed below) is put equal to $n_1 h$, where n_1 is a whole number, known as the "radial" quantum number.

Thus, according to equation (6) on page 179,

$$\int m\dot{r} \,.\, dr = n_1 h,$$

or, introducing the limits $\theta = 0$, and $\theta = 2\pi$,

$$\int_0^{2\pi} m\dot{r} \,.\, \frac{dr}{d\theta} d\theta = n_1 h \quad . \quad . \quad . \quad (31)$$

These two conditions depend upon a certain general quantizing condition, discovered by Sommerfeld and W. Wilson independently.[15] Their ultimate justification must lie in agreement of results deduced from them with experiment.

When these conditions are imposed, and a mathematical argument similar to that given for the circular orbit is employed, it is found that they are sufficient to fix the eccentricity and the lengths of the axes of the ellipse. The negatived energy W in an orbit reduces to the form—

$$W = qZ^2 \frac{1}{(k + n_1)^2} \quad . \quad . \quad . \quad (32)$$

which resembles equation (19) on page 184 for circular orbits. Here q is the same constant as in that equation, and Z is the atomic number of the nucleus. The equations would be identical if—

$$n = k + n_1 \quad . \quad . \quad . \quad . \quad (33)$$

where n is a whole number known as the "total" quantum number of the orbit. In this way, elliptic orbits also give rise to lines of the Balmer type.

In order to fix an elliptic orbit, we must, therefore, specify two quantum numbers, and it is usual to give n and k. The latter is placed as a suffix to the former, as n_k. A 2_1 orbit is such that its total quantum number is 2, and its azimuthal or "subsidiary" quantum number is 1. The radial quantum number can always be derived if required, since by relation (33) above, if any two of the quantities n, k and n_1 are known, the third may be

found. According to equation (32) above, the energy of an orbit depends upon $k + n_1$, i.e. upon n. Thus the total quantum number *defines the energy of an orbit, and there are n orbits of the same energy but differing in eccentricity for a given value of n*. For example, when $n = 4$, the four orbits denoted by 4_4, 4_3, 4_2, and 4_1 correspond, so far as the above argument is concerned, with equal amounts of energy. In the mathematical argument, it is shown that the eccentricity ϵ of the ellipse depends upon n and k according to the relation—

$$n^2(1 - \epsilon^2) = k^2 \quad . \quad . \quad . \quad (34)$$

Thus, when $n = k$, $\epsilon = 0$, so that we have the limiting case of a circular path, and the orbit defined by $n_k = 4_4$ is a circle. Further, when $n = 4$, and k is given the values 3, 2, and 1 in succession, the ellipses increase in eccentricity. In this way, ellipses having the same energy depart more from circular form, the lower the azimuthal quantum number. The case of $k = 0$ need not be considered, for this corresponds with $\epsilon = 1$, which would give motion in a straight line through the nucleus.

Some of the geometrical properties of these orbits may now be considered in the simplest case, namely, that of hydrogen. According to classical mechanics, the energy in an orbit depends, in the case of an elliptic orbit, upon the length of its major axis, or, for a circular orbit, upon that of its diameter. If we call this length $2a$, then (compare equation (15) on p. 183)—

$$W = \frac{e^2}{2a} \quad . \quad . \quad . \quad . \quad (35)$$

for hydrogen, where $Z = 1$. Moreover, W measures the total work done in removing an electron from a given orbit to infinity, so that this work is inversely proportional to the length of the major axis in the case of an elliptic path. Further, equating the values of W given in equations (32) and (35), it follows that:

$$a = \frac{e^2 n^2}{2q} \quad . \quad . \quad . \quad . \quad (36)$$

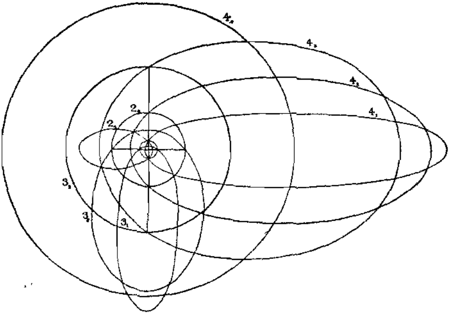
so that a varies as n^2, and the orbits increase very rapidly in size. The group of n orbits of total quantum number n consist of one circle whose radius is given by the above expression, and $(n - 1)$ ellipses having semi-major axes equal to the same amount. Orbits of this type are shown in Fig. 25.

The *periodic time* t in an orbit also depends upon the value of a defined above. It is shown in classical mechanics that t^2 is proportional to a^3, if the inverse square law is obeyed. It has been already observed that this is true for circular orbits (see remarks below equation (26) on page 187). Thus, a increases with total quantum number as $1^2 : 2^2 : 3^2 : 4^2 \ldots$, and t in-

FIGURE XXV

QUANTIZED ELLIPTIC ORBITS

(*Nature*, 1923; 112, 38)



The nucleus is placed at the centre of a circular path, or at one focus of an *elliptical* path of the planetary electron of a hydrogen atom. The greater the eccentricity of an elliptical path, the *nearer* does the electron approach the atomic nucleus. The orbits are defined by certain quantum conditions (*see* text).

creases as $1^3 : 2^3 : 3^3 : 4^3 \ldots$ If n is fixed, the values of a, W, and t are also determined.

The minor axis and *latus rectum* of an elliptic orbit vary in a simple way with changes in the quantum numbers. These lengths depend upon the azimuthal quantum number k. According to geometry of the ellipse, $b^2 = a^2(1 - \epsilon^2)$, where b is the

length of the semi-minor axis. Combining this result with equation (34),

$$1 - \epsilon^2 = \frac{b^2}{a^2} = \frac{k^2}{n^2} \quad . \quad . \quad . \quad (37)$$

Therefore, $b/a = k/n$, or b is the same fraction of a as k is of n. Since k and n are whole numbers, then b will be a simple fractional amount of a. Thus, when k is fixed, b is also fixed.

This may be expressed in a somewhat different way.[16] The azimuthal quantum number k, according to the first quantizing condition and to equation (30), governs the angular momentum, and, therefore, determines the rate of sweeping out equal areas, which can evidently be measured by the area included by an orbit divided by the periodic time, or by πab divided by t. Now t depends only upon a, which is determined by n the total quantum number, and, therefore, when n is fixed, the angular momentum depends only upon b. Consider, then, the two orbits for which n is 2 and k is 2 and 1 respectively. Following Bohr's notation, these two orbits are designated by the symbols 2_2 and 2_1, the former being a circle and the latter an ellipse. According to the first quantizing condition, the rate of sweeping out areas should be twice as great for the 2_2 orbit where $k = 2$ as for the 2_1 orbit where $k = 1$. It follows from this argument that b must be half as great for the 2_1 orbit as for the 2_2 orbit. The latter orbit, however, being circular, has $b = a$, and, therefore, in the 2_1 orbit the minor axis is half the major axis. Similarly, in the orbits 3_2 and 3_1, the values of b are $2a/3$ and $a/3$, and so on.

It follows that, once the azimuthal quantum number k is fixed, the latus rectum of the orbit is also determined, and is the same as the diameter of the circle having a total quantum number n equal to k. It is shown, in the geometry of the ellipse, that the semi-latus rectum l is equal to b^2/a. From equation (37), therefore, it follows that—

$$\frac{l}{a} = \frac{k^2}{n^2} \quad . \quad . \quad . \quad . \quad (38)$$

and, using (33),

$$l = \frac{e^2k^2}{2q} \quad . \quad . \quad . \quad . \quad (39)$$

Thus, l depends upon k exactly as a depends upon n. Fig. 25 and Table XI illustrate this, and the other points mentioned.

It will be seen from the figure that the diameter of the circular path defined by 2_2 is the same as the latus rectum of the path defined by 3_2 or 4_2. The path 2_2 has a major axis equal to the diameter of the path 2_1, and the major axes of 3_2 and 3_1 are equal to the diameter of 3_3, and so on. Further, the minor axis of the orbit 2_1 is one-half of its major axis, that is, one-half of the radius of the circle 2_2, and so on. The following points are thus indicated :—

(1) The number of orbits corresponding to a given total quantum number n is n.

(2) The orbits having the same values of n, but different values of k, have major axes of equal length. They have also the same energies and the same periodic times.

(3) The orbits having the same values of k but different values of n have the same latus rectum, which, when $k = n$, becomes the diameter of a circle. They have also the same angular momenta and the same rates of sweeping out areas.

(4) *In order to specify an orbit, it is necessary to quote* two whole numbers. If the total quantum number and the azimuthal quantum number are given, the major axis and latus rectum are defined. The constant latus rectum of a series of orbits is called by Bohr the constant " parameter."

Table XI shows the relative values of certain functions of circular and elliptic orbits of importance in the present connection. This table may be conveniently studied in conjunction with Fig. 25. The absolute values of many of these orbital attributes may be calculated by using the results given for circular orbits in section 47. Thus, if the radius of the 1_1 circle (K orbit) is taken as 1, then the other lengths, given in columns 6, 7, and 8, are as shown. The absolute radius r of the K orbit in hydrogen is $5{\cdot}32 \times 10^{-9}$ cms., from which the dimensions of other hydrogen orbits may be found. In column 10, the area of the 1_1 circle is taken as 1, whereas it is actually πr^2. (See notes at the foot of the table.)

This discussion of elliptic orbits was introduced by the work of Sommerfeld on the fine structure of the hydrogen lines. The conclusion was drawn that the fine structure might be due to small energy differences between orbits of the same total quantum numbers. The above argument, however, has led to the conclusion *that orbits of the same total quantum number* possess the same energy. It is important to examine whether this view can be absolutely maintained.

The conclusion has been drawn that the lower the azimuthal

TABLE XI

Relative Magnitudes Relating to Circular and Elliptic Orbits

1. Quantum Numbers. Total. n.	2. Azimuthal. k.	3. Radial. n_r.	4. Orbit. n_k.		5. Square of Eccentricity. $\epsilon^2 = \frac{n^2 - k^2}{n^2}$.	6. Semi-Major Axis. $a \propto n^2$.	7. Semi-Minor Axis. $b = \frac{ak}{n}$.	8. Semi-Latus Rectum. $l = \frac{b^2}{a}$.	9. Energy. $E \propto \frac{1}{n^2}$.	10. Area. $A \propto ab$.	11. Periodic Time. $t \propto a^{\frac{3}{2}}$.	12. Angular Momentum. $\propto \frac{A}{t}$.
1	1	0	1_1	Circle .	0	1	1	1	-1	1	1	1
2	2	0	2_2	Circle .	0	4	4	4	$-\frac{1}{4}$	16	8	2
2	1	1	2_1	Ellipse .	$\frac{3}{4}$	4	2	1	$-\frac{1}{4}$	8	8	1
3	3	0	3_3	Circle .	0	9	9	9	$-\frac{1}{9}$	81	27	3
3	2	1	3_2	Ellipse .	$\frac{5}{9}$	9	6	4	$-\frac{1}{9}$	54	27	2
3	1	2	3_1	Ellipse .	$\frac{8}{9}$	9	3	1	$-\frac{1}{9}$	27	27	1
4	4	0	4_4	Circle .	0	16	16	16	$-\frac{1}{16}$	256	64	4
4	3	1	4_3	Ellipse .	$\frac{7}{16}$	16	12	9	$-\frac{1}{16}$	192	64	3
4	2	2	4_2	Ellipse .	$\frac{3}{4}$	16	8	4	$-\frac{1}{16}$	128	64	2
4	1	3	4_1	Ellipse .	$\frac{15}{16}$	16	4	1	$-\frac{1}{16}$	64	64	1

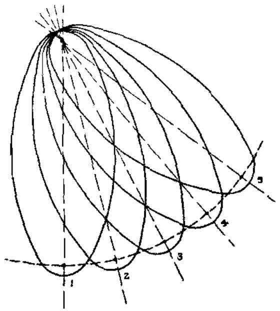
The orbits are defined by the quantum numbers shown in columns 1, 2, 3, and 4. The remaining columns show relative magnitudes; thus, if the radius of the 1_1 circle is taken as unity, then the other lengths are as shown in columns 6, 7, and 8. The area of the 1_1 circle is $ab\pi = \pi$. This is taken as unity for the purpose of column 10. In the last two columns, the periodic time and angular momentum of the 1_1 circle are taken as equal to unity, so that the numbers in the last four columns are only comparable among themselves.

quantum number of an orbit, the greater is its eccentricity, for a given total quantum number. Reference to Fig. 25 and to columns 2 and 5 in Table XI will show this. Thus an electron moving in a 3_1 orbit approaches the nucleus at its nearest point (i.e., at "perihelion") more closely than an electron in a 3_2 orbit. This distance of approach is still further reduced for the 4_1 orbit, and so on. In this way, electrons moving in highly eccentric orbits may be subject to the full charge of the nucleus at short range during perihelion. The effect of this is that they move with high velocities, changing their direction of movement rapidly, and the elliptical shape of the orbit is deformed. It is well known that the theory of relativity gives a better account than that of Newton of the observed motion of the perihelion of the planet Mercury in its orbit round the sun. In somewhat similar fashion, it has been found that when an electron, moving in an orbit of high eccentricity, comes nearest to the nucleus, the motion produced is sufficiently rapid to cause the relativity correction for change of mass with velocity to make an appreciable difference to the energy of the electron in the orbit. This involves, as in the case of Mercury, a slow rotation, or "precession" of the orbit. Movement in an elliptical orbit may, in general, be compounded of two circular motions of equal period, having different phases and opposite directions of motion, as shown in books on physics. In this case, however, the mathematical analysis shows that the relativity correction involves the condition that the ellipse-like motion is compounded of two opposite circular motions of nearly, but not quite the same period, and associated with nearly, but not quite the same energy. The result is that the electron describes a "rosette," so that it is moving in a path which is not truly elliptical. (See Fig. 26.) It has been calculated that the hydrogen electron may make many thousands of complete revolutions round the nucleus before the perihelion has gone round once, so that the effect is a relatively slow one. If, now, these conclusions are admitted, the explanation of the fine structure of hydrogen lines advanced by Sommerfeld follows. On account of orbital precession, orbits of the same total quantum number have not exactly the same energy. The energy of the orbit 2_1, for example, is not quite the same as that of the orbit 2_2, so that an electron jumping from a given outer orbit into the former will radiate energy of slightly different frequency from that of an electron passing from the same outer orbit into the latter. A close doublet in the first line of the Balmer series of hydrogen may, therefore,

be expected. This effect has been observed, working with hydrogen at low temperature. Moreover, the separation in wave-number of the fine lines of H_a were found to correspond closely with the value calculated from this theory of their origin. Similarly, doublets have been observed in the characteristic X-rays of atoms, which have been accounted for in the

FIGURE XXVI

ORBITAL PRECESSION



In the case of elliptic orbits having high eccentricity, the electron approaches the nucleus very closely. This involves a very rapid change of direction of movement, and the *relativity correction for change of mass with velocity* becomes appreciable. A slow rotation or "precession" of the orbit *occurs in consequence. The figure shows* five positions of an orbit of this kind. All intermediate positions are realized, the electron describing a continuous "rosette."

same kind of way. The matter is complicated by the number of possible transitions which may occur. It may be noted that the constant separation of L doublets equals the separation of the first K doublet, for the same atom. This is readily accounted for on the ground that this latter doublet is produced by electrons returning from one or other of the two possible L orbits into the circular K orbit (1_1). The same separation will

evidently result from electrons falling from a given outer orbit into one or other of these two L orbits (2_2 and 2_1). See Fig. 28 on page 204 in this connection.

The theory of spectral series of heavy atoms is not yet satisfactory, so that only certain features which appear to be generally accepted will be noted here. It may be remembered that the spectrum of a more complicated atom exhibits lines which may be grouped into series, characterized by constants S, P, D, and F. It has also been observed that transitions of electrons, when elliptic orbits are included in the scheme, should give rise to lines of the Balmer type. The wave-number of a line should be capable of expression as the difference of two terms, each of which depends upon the reciprocal of the square of a number. The former of these two terms, as in the case of hydrogen, is constant for a given series, and corresponds with the limiting frequency of the series. The wave-number of a line of a series depends upon the energy of the orbit quitted by the electron producing it, i.e., upon the second and variable energy term. When this term is considered, and comparison is made with the hydrogen series, it is found that the S, P, D and F energy terms show a tendency which increases in the order given to approximate to the hydrogen terms. Thus the S terms deviate most, and the F terms least from those of the hydrogen series. The facts in regard to the S terms have been explained on the basis of orbits possessing high eccentricity, and strong "binding," due to the near approach of an electron to a heavy nucleus. It is suggested, further, that the S terms correspond to orbits whose azimuthal quantum number is 1. These eccentric paths are marked by penetration of inner electronic systems by an electron during part of its journey, and by near approach to the positive charge of the nucleus. For the P, D, and F terms, the azimuthal quantum numbers are 2, 3, and 4 respectively. As the azimuthal quantum number is increased, the orbits approximate more to circular form, and tend to lie outside the orbits of lower total quantum number. At the same time, the energies approximate more closely to those of the corresponding hydrogen orbits. These considerations may be conveniently borne in mind in connection with Bohr's general theory of atomic structure (section 50).

In addition to the influence of highly elliptic orbits, two other disturbing influences in the case of heavy atoms should be borne in mind. First, the "screening" effect, which we have discussed in the case of X-ray spectra, will come into

play. The full effect of the nuclear attraction on an electron is diminished by repulsions of other negative electrons. Then, secondly, the inverse square law no longer holds in its simplest form. Sommerfeld has, however, indicated that even when the simple Coulomb field is given up, we obtain, to a first and second approximation, the Rydberg form of the series laws. In this way, a very interesting extension of the theory to heavier atoms was made.

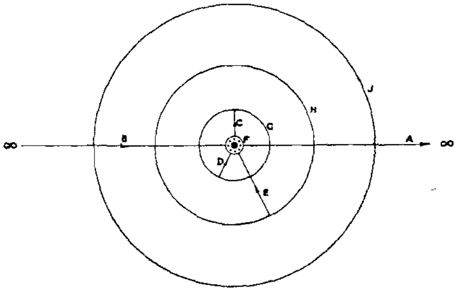
49. Critical Potentials and Absorption Edges

It will be clear from the foregoing that if, according to the Bohr atomic model, energy is emitted when an electron passes from an outer to an inner quantum level, then energy must be supplied to reverse the process and cause the electron to occupy an orbit of higher quantum number. If the energy supplied is gradually increased in amount, a point must ultimately be reached when no more is absorbed. This will correspond to removal of the electron to " infinity," and to ionization of the atom. If the energy is provided by the impact of an external electron which has fallen through a potential of V volts, no absorption should occur if V is below a certain critical value necessary to raise the electron from its normal orbit to the next. For the purposes of the present argument, consider a heavy atom of the type shown in Fig. 27, where a single " valency " electron is in orbit F, in the normal state of the atom. Let an outside electron come into collision with the atom, and let the potential be gradually increased. When the potential reaches a critical value V_1, the energy supplied V_1e is sufficient to move the electron from orbit F to orbit G. The return of this electron will be accompanied by emission of energy of frequency ν_1, where $h\nu_1 = V_1e$, and the emission of a " resonance " line. The potential V_1 is thus a " resonance potential." As V is further increased, other critical states will be reached when the corresponding energies are sufficient to move the electron from the normal orbit F to orbit H or to orbit J and so on. This process has a limit when V becomes the " ionization potential " V_∞ sufficient to remove the electron from the influence of its nucleus. In these circumstances, $V_\infty e = h\nu_\infty$, connecting the ionization potential with the last line of the absorption series, i.e., with the limit of the series. These deductions would appear to be strict consequences of Bohr's theory, and they have been verified by experiment.

Reference to the work of Franck and Hertz has been already made. These investigators were the first to show that a foreign electron colliding with an atom was reflected according to the laws of elastic impact, so long as its energy was below a certain critical value.[17] Further, the quantum relations given above have been verified by numerous workers. Thus, for example,

FIGURE XXVII

IONIZATION, ABSORPTION AND RESONANCE



The central black spot denotes an atomic nucleus carrying charge Ze, the dots round it representing (Z – 1) electrons. The circles F, G, H and J denote stable orbits of an electron. The energy needed to transfer the electron from the innermost orbit F to infinity (as at A) corresponds with the *ionization potential* of the atom. In the same way, B corresponds with the limit of an optical series ("principal" series), and C with the *resonance potential* of the atom. D, E give the first and second lines of the principal series. Energy is emitted when an electron moves from one stable orbit to another nearer the nucleus, and energy is absorbed to reverse the process.

Tate and Foote found agreement in the cases of the resonance and ionization potentials for sodium.[18] The equation $h\nu = Ve$ was tested by inserting experimental values of V and the frequencies of the corresponding lines, also known by experiment. The relation appears to hold for the inert gases and for the vapours of metals such as mercury.

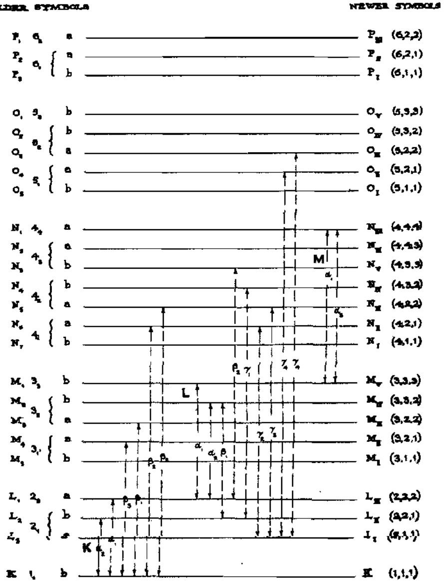
Turning now to X-ray spectra, it has been already noticed that the lines of the K series of an atom cannot be excited separately. As the potential of the X-ray bulb is increased, at a certain critical point, the whole K series appears simultaneously. This leads to the conception of a critical exciting frequency, which is slightly greater than that of any K line. In contrast with the cases of optical spectra considered above, it is not possible to excite the lines of a series separately. This fact finds a ready explanation on the basis of Bohr's hypothesis, when it is recalled that in X-ray spectra the inner electrons of the extranuclear system are involved. An ejected K electron cannot be caught upon an L ring, for example, because that ring is already fully occupied, and contains its full quota of electrons. It is evidently different in the case of optical spectra, where the outer orbits are, in general, unoccupied. But, even in X-ray spectra, it is conceivable that an electron might be removed from the K orbit to one of the unoccupied quantum outer orbits, in which case a line would be actually absorbed. This has been discussed by Kossel.[19] The critical phenomena in relation to X-ray spectra are shown in the observation of edges of absorption bands, studied by de Broglie.[20] As this work has led to other important conclusions, this section will be concluded with a brief consideration of it.

The X-radiation from a metallic anticathode contains a "white" or continuous part, as well as the characteristic lines of the metal. If the continuous rays are reflected from a slowly rotating crystal, a spectrum is obtained, reflection for a given angle of incidence occurring only for the appropriate wavelength. If, now, a thin sheet of a substance containing atoms under investigation is placed in the path of the rays, with a photographic plate on the other side, absorption edges are observed. These edges appear as boundary lines between frequencies absorbed and frequencies transmitted by the substance. It is found in this way that the K series gives one absorption edge, while the L series, when heavier elements are used as transmitting substances, shows three edges.[21] In agreement with this, it is found that there are three critical exciting frequencies, and the complete spectrum is not observed until the highest of these is reached. For the M series, no less than five absorption edges have been detected. Now, since there are three absorption edges for L radiation, it is concluded that there are three different energy levels within the L level, and similarly five energy levels within the M level. It has been

FIGURE XXVIII

ATOMIC ENERGY LEVELS

(*Z. Physik*, 1923; 12, 347)



The "switch" of an electron from an outer to an inner energy level of an atom causes the emission of the corresponding characteristic X-ray line. The levels concerned in the production of a few of the leading lines are inserted in the above diagram (Bohr and Coster). The three quantum numbers shown under the heading "newer symbols" are the total, azimuthal and inner quantum numbers respectively (see text).

found possible to explain the observed frequencies on the basis of energy differences between these levels.[22] Schemes of energy levels have been drawn up for atoms, as illustrated in Fig. 28, which shows the transitions corresponding to some observed X-ray lines. The various levels have been divided into classes, and labelled *a* and *b* in such a way that an electron in radiating energy always passes from an " *a* " level to a " *b* " level, or vice versa. The three L levels may be numbered L_1, L_2, and L_3, the last-named being nearest to the K level. It will be noticed, however, that there are two quantum arrangements for the L level, namely, those corresponding with the orbits 2_2 and 2_1. If these two orbits are called upon to provide three energy levels, it must happen in some way that two different energies correspond with the same quantum numbers, which would demand further explanation. (See section 55, p. 246.)

The important question remains as to whether all theoretically possible transitions can occur. Rubinowicz has put forward a "principle of selection," by which the azimuthal quantum number can only alter by 0, + 1 or − 1 in transitions in atoms of the hydrogen type, removed from the influence of external fields of force.[23] Bohr has reached similar conclusions on the basis of the principle of correspondence, according to which, for very high quantum numbers, the quantum theory of emission passes over into the classical theory; that is, for large quantum numbers where the successive stationary states differ but little in energy, the frequency emitted in the passage of an electron from one orbit to the next lower in quantum number is equal to the frequency of revolution in the orbit. Bohr concludes that the azimuthal quantum number can only change by + 1 or − 1 during a transition. Successful explanations of the intensities and polarization of the observed lines have been made on this basis.

50. Bohr's General Theory of Atomic Structure

This part of the subject would be incomplete without some reference, however brief, to the more recent developments of the dynamic theory of the atom. Bohr has attempted to explain the periodic relationships of elements of higher atomic weights while retaining the explanation of optical line spectra.[24] Bohr's arrangement of the elements has been given (Table I, Frontispiece). Seven vertical columns are shown, which contain

2, 8, 8, 18, 18, 32, and 6 elements respectively, if the spaces corresponding with elements so far undiscovered are counted. Lines are drawn between elements which show distinct resemblances, and certain "interpolated" elements are enclosed in oblong frames. Of these may be mentioned the group of "rare earths," and the elements from scandium to nickel, which tend to resemble each other more than their partners in an earlier group. Bohr has attempted to extend the dynamic theory of the atom in order to cover these facts.

In this more general theory, the binding of successive electrons to the nucleus is considered. An electron added to the outer system of an atom takes up the most stable orbit in the circumstances, that is, the orbit where its firmness of binding is as great as possible. This depends upon the electrons which are already bound. Each electron is provided with an individual orbit, so that electrons in the same orbit as designated by quantum numbers are not thought of as following each other in the same plane, but as having different orbits which can be in different planes. The conception of penetration of outer orbits within orbits which lie as a whole nearer the nucleus is also freely employed, and such penetration is held to involve additional firmness of binding, in the way already suggested. This occurs when an orbit of low azimuthal quantum number is considered. The strength of binding, therefore, does not necessarily vary smoothly with the total quantum number. Thus a 4_1 orbit in the case of calcium (atomic number 20) differs from a 4_1 orbit of hydrogen. The cause of this is the penetration within orbits bound earlier, and the consequent near approach to a nucleus bearing 20 units of positive charge.

The negative electron of the hydrogen atom in its state of firmest binding is assigned the circular 1_1 orbit. The addition of a second electron will produce helium, when the nuclear charge is also increased by one unit. It is supposed that the two systems of spectral lines of neutral helium correspond with different methods of binding the second electron. The normal singlet system is supposed to correspond with a model in which the two electrons move in 1_1 orbits in planes inclined to each other at an angle of 120°. The structure of the helium atom is still uncertain, and the reader is referred to papers by van Vleck and by Millikan.[25] Passing on to the next element (lithium), the third electron is bound in a 2_1 orbit. If a new ring is formed, 2_1 represents a firmer state of binding than 2_2 since 2_1 is elliptical and approaches more closely a nucleus bearing 3 unit

charges. The next three electrons are bound in 2_1 orbits, so that carbon is reached. Following the periodic scheme, the following four electrons are bound in 2_2 orbits, as far as neon. After this, a third ring is commenced, and the total quantum number rises to 3, an increase of this kind occurring after an inert gas is passed. The next element in the scheme is sodium, and a single electron is placed in a 3_1 orbit. The similarity of the alkaline group of metals is explained by each element having a single electron moving in a higher total quantum orbit than any of the previously bound electrons, such that the azimuthal quantum number of this orbit is in each case 1, and penetration of the orbits of the other electrons occurs. Thus lithium, sodium, potassium, rubidium, and caesium commence the 2_1, 3_1, 4_1, 5_1, 6_1 orbits respectively. The following three electrons are bound in 3_1 orbits, and the next four in 3_2 orbits. After argon, the 4 quantum orbits are represented. If this is the case, the 3_3 orbit is passed over, so far as the normal states of the atoms are concerned. The next added electron gives potassium, and is assigned a 4_1 orbit, following the plan adopted in passing from neon to sodium. Another added electron, in a 4_1 orbit, yields calcium, without any electron having entered the 3_3 orbit. At this stage, however, further increase in nuclear charge increases the firmness of binding in the 3_3 orbit. Evidence is brought forward from the spark spectrum of calcium. It is found that in this case the first energy term of the D series is only slightly less than that of the first term of the S series. But, according to ideas already mentioned, these terms correspond with the 3_3 and 4_1 orbits respectively, so that a point appears to have been reached in which the energy of the 3_3 orbit has become only slightly less than that of the 4_1 orbit. Thus the firmness of binding in the 3_3 orbit seems to have been gradually increased by the addition of two 4_1 orbits, and, therefore, the next added electron occupies the 3_3 orbit, and scandium is reached. This is a new feature: a stage of lower quantum number has been passed over as representing weaker binding, and only begins to be filled when its firmness of binding has been sufficiently increased. Bohr argues that the process of internal building continues until there are 6 electrons in each of the orbits 3_1, 3_2, and 3_3, and that it is associated with the increasing resemblance of the group of elements from scandium to nickel and with the development of ferromagnetic properties. In a similar way, the existence of the group of rare earths is attributed to the building up of orbits of total quantum number

4 after the 5 quantum group has been commenced. The max mum number of electrons placed in an orbit n_k is $2n$. The wa in which orbits are assigned to the electrons in the inert ga group of elements is shown in the following table: —

TABLE XII

Electronic Orbits in Inert Gas Group

	Z.	1_1.	2_1.	2_2.	3_1.	3_2.	3_3.	4_1.	4_2.	4_3.	4_4.	5_1.	5_2.	5_3.	6_1.	6_2.
Helium .	2	2														
Neon .	10	2	4	4												
Argon .	18	2	4	4	4	4										
Krypton .	36	2	4	4	6	6	6	4	4							
Xenon .	54	2	4	4	6	6	6	6	6	6		4	4			
Niton .	86	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4

The *inert gases* (*except helium*) *have 8 electrons in thei highest quantum orbit.* Further, the maximum total numbe of electrons in an n-quantum orbit is $2n^2$.

Four forms of growth are postulated, as the binding process proceeds.

(1) The first step is the establishment of the two 2_1 orbits of helium. (2) Next, two orbits of 4 electrons each are set up. This occurs from lithium (3) to neon (10), from sodium (11) to argon (18), from copper (29) to krypton (36), from silver (47) to xenon (54), and from gold (79) to niton (86). (3) After we pass calcium, a sub-group of 4, 4 expands to 6, 6, 6, between scandium (21) and nickel (28). The same occurs from yttrium (39) to palladium (46), and from lutecium (71) to platinum (78). (4) *A fourth type of development occurs in the formation of the rare earth group.* From cerium (58) to lutecium (71), a group of 6, 6, 6 expands to 8, 8, 8, 8. There are thus $(4 \times 8) - (3 \times 6) = 14$ rare earths.

In concluding this account of Bohr's generalized theory, an instance of the way in which it explains experimental results may be given in the case of sodium (11). The electrons are placed as follows:—

Orbit . . .	1_1	2_1	2_2	3_1
Number of electrons .	2	4	4	1

According to the theory, the eleventh electron is more firmly bound than one in a 3_1 orbit of hydrogen. This orbit in sodium gives rise to the first energy term of the S series. This term, therefore, deviates considerably from the corresponding hydrogen term, as experiment shows. On the other hand, a 3_3 orbit of sodium (not represented in the normal state of the atom) will tend to resemble the 3_3 orbit of hydrogen, since it is circular and lies outside the orbits of the 10 electrons previously bound. The first energy term of the D series (where $k = 3$) may be expected to correspond more closely with the hydrogen term, and this is also observed. Further, the first term of the P series, corresponding with the intermediate orbit 3_2, is found to give rise to an energy term which deviates from the hydrogen term more than the first D term, but less than the first S term. Reference to section 48, page 200, will possibly make this matter clearer. It is there suggested that the terms of the S, P, D, and F series correspond with values of the azimuthal quantum number k which are 1, 2, 3, and 4 respectively. Similar reasoning may be applied in considering the optical spectra of other elements.

While Bohr's theory has thus met with success in explaining much in relation to atoms, when molecules are considered, it is found that even in the simplest case, that of hydrogen, no generally acceptable model has been proposed. The model proposed by Bohr has met with difficulties in explaining the molecular heats of hydrogen at different temperatures, the heat of dissociation into atoms and its diamagnetic nature. The difficulties in the way of extension to compounds are doubtless very great. The Bohr model, however, has explained many of the things in which the physicist is most interested. The chemist, on the other hand, approaches the problem rather from the point of view of combination between atoms. The problem of atomic structure shows the fusion of two different habits of thought, and neither chemist nor physicist can live to-day in perfect peace of mind in his own water-tight compartment. The problem must next be treated from the point of view of the chemist, and it will be seen that the contributions which have been made to the fuller understanding of the subject are exceedingly diverse, and of considerable general importance.

REFERENCES: (VIII)

See Nos. 9, 11, 13, 14, 16, 18 *and* 20 *in Bibliographical List at end of book*

1 (p. 168) J. J. THOMSON: "On the Structure of the Atom"; *Phil. Mag.*, 1904; (vi.) **7**, 237.

2 (p. 168) J. J. THOMSON: "Cathode Rays"; *Phil. Mag.*, 1897; (v.) **44**, 298.

J. K. MARSH and A. W. STEWART: "A Magnetic Model of Atomic Constitution"; *Nature*, 1922; **109**, 340.

3 (p. 169) W. L. BRAGG: "Atomic Arrangement in Crystals"; *Phil. Mag.*, 1920; (vi.) **40**, 169.

Idem with H. BELL: "The Dimensions of Atoms and Molecules"; *Nature*, 1921; **107**, 107.

4 (p. 169) E. WAGNER: "Spektraluntersuchungen an Röntgenstrahlen"; *Ann. Phys.*, 1915; (iv.) **46**, 868.

M. SIEGBAHN: "Relations between the K and L Series of the High Frequency Spectra"; *Nature*, 1916; **96**, 676.

5 (p. 169) E. WAGNER: "Atombau and Röntgenspektra"; *Z. Elektrochem.*, 1920; **26**, 260.

6 (p. 170) M. SIEGBAHN: "Bericht uber die letzte Entwicklung der Röntgenspektroskopie"; *Jahr. Rad. Elekt.*, 1921; **18**, 240. This Paper contains a useful list of references.

7 (p. 171) A. A. MICHELSON: "On the Application of Interference Methods to Spectroscopic Measurements"; *Phil. Mag.*, 1891; (v.) **31**, 338: 1892; (v.) **34**, 280.

8 (p. 172) T. R. MERTON and S. BARRATT: "On the Spectrum of Hydrogen"; *Phil. Trans.*, 1922; **A222**, 369.

9 (p. 172) J. J. BALMER: "Notiz über die Spektrallinien des Wasserstoffs"; *Wied. Ann.*, 1885; **25**, 80.

10 (p. 173) A. FOWLER: "Series Lines in Spark Spectra"; *Phil. Trans.*, 1914; **A214**, 225: *Proc. Roy. Soc.*, 1914; **A90**, 426: *Nature* 1914; **93**, 145.

N BOHR, A. FOWLER: "The Spectra of Helium and Hydrogen"; *Nature*, 1913; **92**, 231.

11 (p. 173) W. RITZ: "Über ein neues Gesetz der Serienspektren"; *Phys. Z.*, 1908; **9**, 521.

12 (p. 175) N. BOHR: "On the Constitution of Atoms and Molecules"; *Phil. Mag.*, 1913; (iv.) **26**, 1, 476, 857.

Idem: "On the Quantum Theory of Radiation, and the Structure of the Atom"; *Phil. Mag.*, 1915; (vi.) **30**, 394.

13 (p. 181) G. H. LIVENS: "Does an accelerated Electron necessarily radiate Energy on the Classical Theory?"; *Phil. Mag.*, 1921; (vi.) **42**, 807. See also G. A. SCHOTT: *Phil. Mag.*, 1923; (vi.) **45**, 769.

14 (p. 189) A. SOMMERFELD: "Zur Quantentheorie der Spektrallinien"; *Ann. Physik*, 1916; (iv.) **51**, 1.

15 (p. 192) W. WILSON: "The Quantum Theory of Radiation and Line Spectra"; *Phil. Mag.*, 1915; (vi.) **29**, 795. See also last Ref., and A. SOMMERFELD: "Grundlagen und Ziele der Bohrschen Theorie von Atomen und Spektren"; *Z. Elektrochem.*, 1920; **26**, 258.

16 (p. 195) O. LODGE: "The Kinetic Atom"; *Nature*, 1924; **113**, 15.

17 (p. 202) J. FRANCK and G. HERTZ: "Die Bestätigung der Bohrschen Atomtheorie im optischen Spektrum durch Untersuchungen der unelastischen Zusammenstösse langsamer Electronen mit Gasmolekülen"; *Phys. Z.*, 1919; **20**, 132. See also *ibid.*, p. 481.
18 (p. 202) J. T. TATE and P. D. FOOTE: "Resonance and Ionisation Potentials for Electrons in Metallic Vapours"; *Phil. Mag.*, 1918; (vi.) **36**, 64.
19 (p. 203) W. KOSSEL: "Zum Bau der Röntgenspektren"; *Z. Physik*, 1920; **1**, 119.
20 (p. 203) M. de BROGLIE: "Sur la spectroscopie des rayons secondaires émis hors des tubes à rayons de Röntgen, et les spectres d'absorption"; *Compt. Rend.*, 1914; **158**, 1493.
21 (p. 203) *Idem*: "Sur la bande d'absorption K des éléments pour les rayons X suivie du brom au bismuth, et l'émission d'un tube Coolidge vers les très courtes longueurs d'onde"; *Compt. Rend.*, 1916; **163**, 87.
Idem: "Sur un système d'absorption correspondant aux rayons L des spectres de rayons X des éléments, et sur l'importance des phénomènes d'absorption sélective en radiographie"; *Compt. Rend.*, 1916; **163**, 352. See also: H. ROBINSON: "The Secondary Corpuscular Rays produced by Homogeneous X-Rays"; *Proc. Roy. Soc.*, 1923; **A104**, 455.
22 (p. 205) D. COSTER: "On the Spectra of X-Rays and the Theory of Atomic Structure"; *Phil. Mag.*, 1922; (vi.) **43**, 1070.
23 (p. 205) A. RUBINOWICZ: "Bohrsche Frequenzbedingung und Erhaltung des Impulsmomentes"; *Phys. Z.*, 1918; **19**, 441, 465.
24 (p. 205) N. BOHR: "Atomic Structure"; *Nature*; **107**, 104: **108**, 208.
Idem: "The Structure of the Atom"; *Nature*, 1923; **112**, 29.
Idem: "Der Bau der Atome und die physikalischen und chemischen Eigenschaften der Elemente"; *Z. Physik*, 1922; **9**, 1.
Idem: "Über die Anwendung der Quantentheorie auf den Atombau"; *Z. Physik*, 1923; **13**, 117.
Idem: "Linienspektren und Atombau"; *Ann. Physik*, 1923; (iv.) **71**, 229.
25 (p. 206) J. H. VAN VLECK: "The Dilemma of the Helium Atom"; *Phys. Rev.*, 1922; (ii.) **19**, 419.
R. A. MILLIKAN: "Some Facts bearing on the Structure of Atoms, particularly of the Helium Atom"; *Phys. Rev.*, 1921; (ii.) **18**, 456. See also I. LANGMUIR: *Science*, 1920; **51**, 605.

CHAPTER IX

ATOMIC ARCHITECTURE: (3) THE EXTRANUCLEAR ELECTRONS IN COMBINATION

51. General Principles

IT has been emphasized by several authors that any theory advanced to explain the combination of atoms to form compounds must take into account the existence of compounds of two types, now generally known as "polar" and "non-polar," or as "heteropolar" and "homopolar" respectively. This broad division into classes is characterized by the presence or absence of ionization. Thus, inorganic compounds fall largely into the polar class and organic compounds into the non-polar class. The importance of a division of this kind was brought out in the writings of Thomson, G. N. Lewis and Kossel.

In the course of his work on positive rays, Thomson found that negatively-charged particles were present in the stream, in a discharge tube. These particles must have been positively charged originally, and later attracted two or more negative electrons. Thomson suggested that if an atom could behave thus in such unfavourable circumstances, it was very improbable that the same kind of atom in combination should be unable to extract a negative charge from another atom when the kind of combination was suitable.[1] He had observed negative charges on the particles when hydrogen, oxygen, carbon and chlorine were present in the tube. Thus, some compounds of these elements might reasonably be expected to have polarized molecules, or "ionic molecules," the latter being the term actually suggested by Thomson. The process by which an ionic molecule was formed was referred to as "intramolecular ionization." As a criterion, measurements of specific inductive capacities were employed. It was argued that ionic molecules would necessarily possess large electrical moments, which would

be marked by large specific inductive capacities. If the relation $K = n^2$ was obeyed (where n was the refractive index) in a particular case, the compound was classed as having no intramolecular ionization; while if the value of K was greater than that required by the above relation, the compound was placed in the ionized class. In this way, the following table was obtained:—

TABLE XIII

Groups of Ionized and Non-ionized Molecules

GROUP 1. Not Ionized.	GROUP 2. Ionized.
H_2, O_2, N_2, Cl_2, CO, CO_2, He, CS_2, CH_4, CCl_4, C_6H_6, N_2O.	HCl, CH_3Cl, $CHCl_3$ (weak), H_2O, CH_3OH, C_2H_5OH, NH_3, SO_2.

G. N. Lewis independently drew attention to the existence of two types of molecules, the distinction being marked, not only by the presence or absence of ionization, but also by a more general divergence in properties, as the following table, abridged from his paper, shows:—[8]

TABLE XIV

Properties of Polar and Non-polar Molecules

Polar.	Non-polar.
Reactive.	Inert.
Tautomerism.	Isomerism.
Ionized.	Not ionized.
Ionizing solvents.	Not ionizing solvents.
High dielectric constant.	*Low dielectric constant.*
Molecular complexes.	No molecular complexes.
Association.	No association.

The two classes of compounds correspond with types of combination distinguished by Briggs in 1908. As an example of a typical ionized and polar molecule, lithium fluoride may be taken, *where a positive and a negative element combine.* The evidence supplied by the X-ray method leads to the conclusion that this compound is ionized in the crystalline state. On the other hand, molecular fluorine may be taken as a type of non-polar combination, the molecule being formed by the union of two like negative atoms of fluorine. The division into polar and non-polar is strongly indicated by the work on crystal structure (section 17).

A theory of chemical combination must also be profoundly

influenced by the regularities shown by the periodic classification of the elements. In 1916, Lewis[3] and Kossel[4] independently drew attention to the stability of the inert gas group of elements, as indicating electronic configurations which electrons in other atoms would tend to assume. Thus the electropositiveness of potassium could be explained by a tendency to give up one electron, with the formation of a positive ion having an outer sheath like that of argon. In similar fashion, chlorine is electronegative on account of its tendency to take up an electron, giving the same outer arrangement as that of the potassium ion. The chlorine ion is negatively charged, since the neutral atom gains a negative electron, and the potassium ion is positively charged, since the neutral atom loses a negative electron. This accords with the respective atomic numbers: chlorine (17), argon (18), and potassium (19). An atom of argon differs from an ion of potassium in having one positive charge less on its nucleus, and from an ion of chlorine in having one charge more. An atom of potassium may thus be considered as having one "valency" electron, and an atom of chlorine seven valency electrons. Apart from these electrons, an atom has a positively charged residue which remains unchanged in chemical changes, which was termed by Lewis the "kernel" of the atom. The valency electrons take part in chemical combination and may be thought of as constituting the "sheath" or "shell." In this way, the potassium ion may be regarded as having no sheath, and the chlorine ion a completed sheath. Solid potassium chloride consists of the two kinds of ions in a crystal lattice. Solution in water causes the breakdown of this lattice and consequent freedom of the ions.

The same element may, however, exert positive and negative valencies in different compounds, which are such that, according to Abegg's rule, the sum of the maximum positive and maximum negative valencies is equal to 8.[5] Thus chlorine exerts a positive valency of 7 in Cl_2O_7, as well as a negative valency of 1 in KCl. This is explained by the number of outer electrons in the case of the inert gases being 8, a number representing a stable arrangement, without any tendency to take or to give up electrons, so that no compounds are formed in this group. Chlorine is given 7 outer valency sheath electrons, and can either take up one electron to form a positive ion with the stable argon grouping, or lose the 7 electrons, and form a negative ion with the stable grouping of neon. Similarly, oxygen with an outer shell of 6 electrons would be expected to manifest a negative valency

of 2 or a positive valency of 6, according as it gains 2 electrons and forms the neon grouping or loses 6 electrons and forms the helium arrangement. The normal valency of an atom (e.g., + 1 for potassium, and − 1 for chlorine) is termed its "principal" valency; chlorine also shows a "contravalency" of + 7. These numbers refer to maximum positive or negative valencies; an atom may not exert its full valency in all cases. Thus, according to Lewis' second postulate, an atom consists of a kernel together with a shell, the number of electrons in the latter varying from 0 to 8. The first postulate defines the kernel as follows: "*In every atom is an essential kernel which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.*"

Lewis also called attention to the fact that the numbers of shell electrons in molecules are frequently equal to 8 or simple multiples of 8. Thus, for example, in lithium fluoride, lithium has 1 shell electron and fluorine 7, making a total of 8. In magnesium chloride, divalent magnesium has 2 shell electrons and chlorine 7, so that in $MgCl_2$ we have $2 + (2 \times 7) = 16$, or 8×2 shell electrons. Again, in sodium nitrate $NaNO_3$, there are $1 + 5 + (3 \times 6) = 24$, or 8×3 shell electrons, and so on. In general, the number of shell electrons in compounds tends to be even, so that sulphur dioxide SO_2 has 18 and sodium hypochlorite NaClO 14 electrons. There are a few exceptional cases, but these are compounds of high reactivity; for example, nitric oxide NO has 11, nitrogen peroxide NO_2 17, and chlorine dioxide ClO_2 19 shell electrons. These results were embodied in a third postulate, which stated that a molecule tends to hold an even number of electrons in the shells of its component atoms, and especially to hold 8 electrons. It was here that the cubical atom made its appearance, for the suggestion was made that the stable arrangement of 8 electrons was that of the cube. Thus, 8 electrons placed at the corners of a cube was postulated as the stable grouping of the inert gases of the helium series. Helium itself, of course, cannot have this arrangement, as 2 electrons only are available, and the first completed cube appears with neon, atomic number 10. After helium, lithium has a third electron in a new shell, just as in Bohr's model the 2-quantum orbits begin at this point. The next element, beryllium, has 2 inner and 2 outer electrons, and so on, till we reach neon, where a cube is complete. After this, sodium begins another

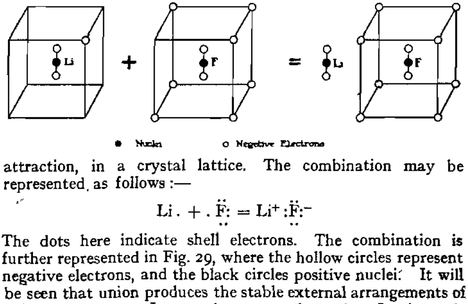
shell with a single outer electron, and, therefore, resembles lithium. The continual addition of electrons completes the second short period of elements with argon, atomic number 18, where a second cube is complete.

Lewis' explanation of the two kinds of chemical union, polar and non-polar, will now be given, taking lithium fluoride and molecular fluorine as examples of the two types. In lithium fluorine there are 3 electrons, arranged as 2, 1; whereas in fluorine there are 9 electrons, arranged as 2, 7. Combination occurs by lithium supplying the electron needed to complete the cube of fluorine. The transference of the electron gives a positively charged lithium ion and a negatively charged fluorine ion. In the compound these are held together by electrostatic

FIGURE XXIX

POLAR COMBINATION—LITHIUM FLUORIDE (LEWIS)

(See *J. Amer. Chem. Soc.*, 1916; 38, 775 *seq.*)



attraction, in a crystal lattice. The combination may be represented as follows :—

$$\mathrm{Li}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}: = \mathrm{Li}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:^{-}$$

The dots here indicate shell electrons. The combination is further represented in Fig. 29, where the hollow circles represent negative electrons, and the black circles positive nuclei. It will be seen that union produces the stable external arrangements of helium and neon. In regard to non-polar union, Lewis made an extremely fertile suggestion, which was embodied in a fourth postulate, stating that atomic shells were interpenetratable. Since an atom of fluorine contains 7 shell electrons, union between two atoms to form a molecule can occur by 2 electrons being *shared* with the completion of two cubes. Thus—

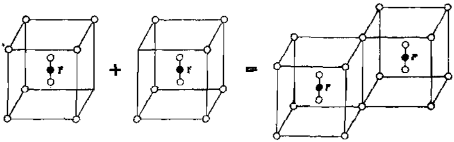
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}: = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{F}}}:$$

or, in three dimensions, the union occurs as in Fig. 30. In this way, the conception of cubic stability is retained, the two cubes sharing a common edge. Similarly, hydrogen and water may be written *in one plane* as H : H and $\text{H} : \underset{\cdot\cdot}{\ddot{\text{O}}} : \text{H}$ *respectively.*

FIGURE XXX

NON-POLAR COMBINATION. I. FLUORINE MOLECULE (LEWIS)

(*J. Amer. Chem. Soc.*, 1916; 38, 775)

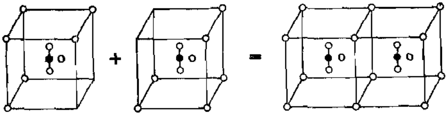


In many cases, such formulæ may represent only one of several possible tautomeric forms. Molecular oxygen may be formed on the assumption that two pairs of electrons are shared, so that two cubes are formed which are in contact along one face

FIGURE XXXI

NON-POLAR COMBINATION. II. OXYGEN MOLECULE (LEWIS)

(*J. Amer. Chem. Soc.*, 1916; 38, 778)



of each cube. Thus, oxygen has 6 shell electrons, so that union occurs as follows :—

$$:\ddot{\text{O}}: + :\ddot{\text{O}}: = :\ddot{\text{O}}::\ddot{\text{O}}:$$

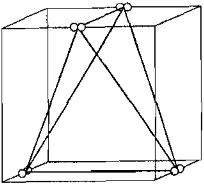
This is represented in Fig. 31, which shows Lewis' representation of a double bond in O = O. It is to be noted that non-polar

union is restricted to combination between *negative* atoms, which, having a deficiency of electrons, can complete each other's cubes by sharing. On considering the triple bond, however, it is clear that no simple explanation can be given on the basis of a cube theory without modification, since three edges of a cube cannot be shared with another cube. Lewis supposed that the electrons of a cube may tend to approach one another in pairs, forming a tetrahedral arrangement, as shown in Fig. 32. In this figure, the helium electrons are omitted, and in further diagrams shells only will be shown.

FIGURE XXXII

TETRAHEDRAL ARRANGEMENT OF ELECTRONS (LEWIS)

(*J. Amer. Chem. Soc.*, 1916; 38, 780)



The electrons at the eight corners of a cube are supposed to be drawn together in pairs, thereby producing a tetrahedral arrangement. By this means, a model of the carbon atom is obtained, and an explanation is found of the triple bond in chemical combination.

It seems difficult to imagine why electrons should approach each other in this way, though magnetic forces could be postulated. If, however, the result is assumed, then an interpretation of the triple bond is obtained by the interfacial contact of two tetrahedra. In all these cases, the models are essentially "static," so that no movement of the electrons is postulated.

Coming next to the contributions of Kossel, it is important to observe that, beside emphasizing the nature of polar and non-polar combination and the stability of the inert gas elements, he attempted to account for the firmness of union in compounds on the basis of the charges and volumes of ions concerned.[1]

The atom was thought of as a smooth sphere, having a charge at its centre of gravity. The negative electrons of the extranuclear system were not pictured as at rest, but as moving in concentric orbits in a plane. The smallness of the hydrogen ion enabled it to get close to a negative partner. In Fig. 33, this ion is denoted by ⊕, and the series shows a steadily decreasing stability of combination. In the first three cases, if the central negative group is assumed to have approximately the same size, the stability decreases because a smaller negative charge is distributed over the same surface. In IV, however, the same

FIGURE XXXIII

GROUPS OF VARYING STABILITY (KOSSEL)

(Ann. Physik, 1916; (iv) 49, 270)

I. II. III. IV.

negative charge as in III is distributed over a greater surface, so that the grouping is still less stable. Thus, the larger the central charge and the smaller the volume of its atomic sphere, the greater is the attractive force, and the greater the tendency to form complex molecules. In the series NH_3, PH_3, AsH_3, SbH_3, the volume of the central atom increases, with corresponding decrease in stability. In Table XV, NH_3 shows the greatest stability and HI the least.

TABLE XV

Stabilities of the Hydrides of the Elements

↑ Increasing Stability	NH_3	OH_2	FH	↓ Increasing Volume
	PH_3	SH_2	ClH	
	AsH_3	SeH_2	BrH	
	SbH_3	TeH_2	IH	

← Increasing Stability
→ Decreasing Charge

Thus, H_2O can remove an H^+ (ion) from all hydrides below it and to the right of it; for example,

$$H_2O + HF = F^- + H_2O . H^+$$

since the central charge in HF is smaller than that in OH_2, and distributed upon approximately the same sphere. Thus the compounds coming after water in the list are acids. On the other hand, NH_3 acts as a base, since, according to the same reasoning, it can extract an H^+ from water :—

$$H_2O + NH_3 = NH_4^+ + OH^-$$

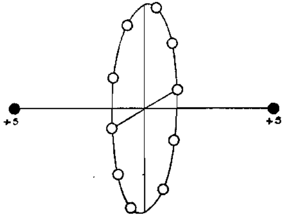
PH_3 does not do this, because the volume of the central atom is greater than that in NH_3, so that it does not exert so large an attraction upon the H^+ of water. This forms a basis for theories of acids and bases, which will be treated in section 54.

Kossel gave the nitrogen molecule the arrangement shown

FIGURE XXXIV

NITROGEN MOLECULE (KOSSEL)

(*Ann. Physik*, 1916; (iv) 49, 359)



in Fig. 34, where ten electrons follow each other in the same orbit.

In considering the fundamental principles of the relation of electron theory to the chemical properties of atoms and molecules, special honour belongs to Thomson in having first formulated a theory to connect these matters as early as 1904, before the discovery of the atomic nucleus.[6] He considered the arrangement of electrons concentrically in a sphere of uniform positive electrification. Later, he drew attention to the fact that the outer electrons of an atom were the most mobile, being held in their places less firmly than the inner electrons, so that they would be more readily influenced by neighbouring atoms, and be concerned in chemical combination, and in all the

"constitutive" properties of the atom, such as surface tension, viscosity and cohesion.[7] The properties which are associated with that part of the atom which is unchanged in combination (the kernel of Lewis) are "intrinsic" and vary continuously from one atom to the next, whereas the constitutive properties vary periodically as the valency does.

Thomson has also considered a law of force within the atom different from the simple law of the inverse square assumed by Bohr.[8] Thus, while Bohr attained stability in the atom by quantizing the orbits, Thomson preferred to assume an attractive force acting under the inverse square law and a repulsive force inversely proportional to the cube of the distance r. The resultant force F could be written :—

$$F = \frac{Ze^2}{r^2}\left(1 - \frac{C}{r}\right) \qquad . \quad . \quad . \quad (1)$$

where C is a constant, Z the atomic number and e the electronic charge. By means of this assumption, he calculated the ratio of the charge on the nucleus Ze to the electronic charge e necessary to hold n electrons symmetrically in three dimensions, as follows :—

n.	Ze/e.	n.	Ze/e.
1	0·70	6	4·8
2	0·75	8	7·6
3	1·58	12	13
4	2·44	20	30

It will be seen that if more than eight electrons are held, the nuclear charge is greater than the charges on the negative electrons. This provides a mathematical basis for the cube theory. Thomson also drew attention to the fact that in positive ray analysis, the greatest charge ever observed on an ion is 8, and that it was impossible to give a negative charge to an inert gas of the argon series. Further, following Föppl, Thomson considered that the stable arrangement of eight electrons was not the cube but a "twisted" cube, as represented in Fig. 35. This allows for the sharing of 2, 3, or 4 electrons, since the solid figure obtained has triangular as well as square faces. In this way, the anomalous case of ClO_2, where there are 19 shell electrons, can be explained by supposing that an oxygen atom is linked to chlorine by a triangular face held in common, and to the other oxygen atom by an edge. In this way, three

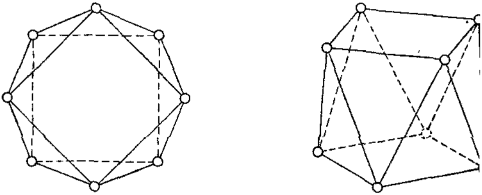
twisted cubes are joined, as will be seen if a model is made. The arrangement may be represented by $:\ddot{Cl}:\ddot{O}:\ddot{O}:$.

This preliminary discussion may be concluded by noticing that by means of the law of force given in equation (1) above, Thomson deduced a relation of the same type as that of Planck ($\epsilon = h\nu$).[9]

FIGURE XXXV

TWISTED CUBE ATOM (THOMSON)

(*Phil. Mag.*, 1921; (vi) **41**, 515)



The first diagram shows the model in plan, and the second in perspective.

52. The Theory of Langmuir

The observation that the atomic number of a member of the group of inert gases is given by the following expression, by stopping at any term, was made by Rydberg:—[10]

$$Z = 2(1 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2) \quad . \quad . \quad (2)$$

Thus, supposing that a new shell of electrons begins after the completion of the former shell at an inert gas, the following series for the numbers of electrons in successive shells of the niton atom (atomic number 86) is reached: 2, 8, 8, 18, 18, 32. This is not the same as the result of Bohr's considerations according to total quantum numbers (see Table XII, on p. 208): 2, 8, 18, 32, 18, 8. Langmuir, however, has assumed that electrons are built up continuously in shells, according to the former arrangement, each shell being completed before the next one is commenced, so that a new electron is always added to

the outermost shell.[11] This theory is based upon the static model of Lewis discussed in the previous section.

The original theory contained a large number of postulates, which have since been reduced to three, as follows :—[12]

Postulate 1.—The electrons tend to be arranged on the surfaces of concentric spheres, which contain successively 2, 8, 8, 18, 18, and 32 electrons.

Postulate 2.—Atoms may be coupled together by one or more pairs of electrons (duplets), which are held in common in the completed sheaths of the atoms.

Postulate 3.—The residual charge on each atom and on each group of atoms tends to a minimum.

The latter postulate is the only one likely to present any difficulty. It really limits the operation of the first postulate, which marks a tendency for electricity to accumulate on the surface of atoms. Thus, in any compound where ions are formed, it is clear that the tendency of Postulate 1 predominates. According to Postulate 3, however, the ions when formed will tend to be held together to form a neutral body. Again, an element in the middle of a series of 18, such as nickel with 28 electrons, may form quite stable compounds without building up the krypton formation of 36 electrons, nickel chloride $NiCl_2$, where the nickel ion has 26 electrons, being stable. In this case, it may be supposed that the third postulate is operative.

In the original paper, Langmuir distinguished between shells and layers, and made certain assumptions regarding the radii of the shells. These assumptions appear, however, to be quite unnecessary, and in no way affect the conclusions of the theory.

Langmuir's theory, like that of Lewis, is essentially a static theory. If the outer electrons are in motion, nothing more than oscillation about a mean position is postulated, so that the basis of this theory seems essentially different from that of Bohr. Whether any agreement between the two conceptions exists will be considered later.

A fundamental equation, which Langmuir has applied to many compounds, must now be given. If E is the total number of shell electrons of the atoms forming a compound, n the number of completed "octets," and p the number of duplets (except those with hydrogen), a little consideration will show that when octets only are concerned,

$$E = 8n - 2p \quad . \quad . \quad . \quad . \quad (3)$$

or, rearranging,

$$p = \frac{1}{2}(8n - E) \quad . \quad . \quad . \quad . \quad (4)$$

The limitation with regard to hydrogen is interesting. Lowry has drawn special attention to the fact that it is often difficult to decide whether hydrogen is linked by a " covalency " (non-polar link) or an " electrovalency " (polar link).[13] This is because hydrogen ionizes uniquely into a bare nucleus without any external system.

Equation (4) above may now be applied in a few simple cases. For water, $E = 8$ $(6 + 1 + 1)$, $n = 1$, therefore $p = 0$, giving one complete octet with two external hydrogen nuclei. For molecular chlorine, $E = 14$ $(7 + 7)$, $n = 2$, so that $p = 1$. This corresponds with the single covalent bond, as in Fig. 30, where molecular fluorine is shown. Molecular oxygen has $E = 12$, $n = 2$, so that $p = 2$, corresponding with the double bond of Fig. 31. As a further example, consider acetic acid, where $E = 24$, $n = 4$, so that $p = 4$. The central carbon is linked by a double bond to one oxygen, giving $p = 2$, and shares an edge with the other oxygen atom and another edge with the carbon of the CH_3 group, making $p = 4$ as required. The structure of acetic acid on this basis is shown in Fig. 36.

The terms " covalency " and " electrovalency " were introduced by Langmuir to distinguish between non-polar and polar combination. The covalency of an atom may be defined as the number of electron pairs shared with adjacent atoms. The electrovalency of an atom is either positive or negative, the former corresponding with the number of electrons lost by the neutral atom in forming a compound, and the latter with the number of electrons gained in this way.

Langmuir also attempted to correlate physical properties with electronic structure. For example, when the external " stray " field of a molecule is small (that is, where Postulate 3 *is strongly operative) the cohesion between neighbouring mole*cules is small, and the boiling-point is, therefore, low.

With regard to the operation of the postulates, Langmuir has divided compounds into three classes. Thus the first class consists of " complete " compounds, where Postulate 1 is satisfied. The second class contains " incomplete " compounds, where the tendency of Postulate 1 is not achieved. Into this class fall intermetallic compounds and compounds of elements in the middle of long series, such as ZnO, Fe_3O_4, PbS, $NiCl_2$, and CuO.

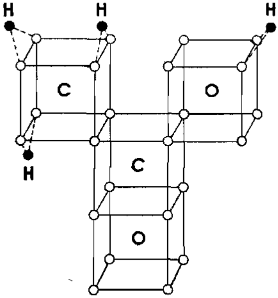
For example, zinc, atomic number 30, has shells of 2, 8, 8, 12 electrons according to the postulate. In zinc oxide, therefore, the outer shell is incompletely filled, since 18 electrons are required. Lastly, a third class contains exceptional cases, of which may be mentioned N_2, CO, N_2O, BH_3 and "molecular" compounds and the ion CN^-. This class demands special attention here.

The inertness of nitrogen in the free state and its extreme reactivity in combination has always been somewhat of a mystery. Moreover, nitrogen resembles carbon monoxide in

FIGURE XXXVI

STRUCTURE OF ACETIC ACID (LANGMUIR)

(*J. Amer. Chem. Soc.*, 1919; 41, 896)



physical properties in a remarkable way, and nitrous oxide (N_2O) resembles carbon dioxide (CO_2) in all physical properties except that of freezing-point. This resemblance is shown in the case of nitrogen and carbon monoxide in Table XVI. It would appear that such remarkable agreement must correspond with similarity of molecular structure. A little consideration shows that the number of sheath electrons in each case is 10. Langmuir suggested the structure shown in Fig. 37 for the two cases. The sole difference is the inequality of nuclear charges in the case of carbon monoxide, which leads to a state

of lower stability. It is also well known that the ion CN^- resembles *the ion* Cl^- *remarkably. Here the number of sheath* electrons is again 10, so by placing both nuclei within one octet

TABLE XVI

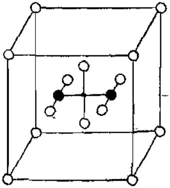
Comparison of Physical Properties of Nitrogen and Carbon Monoxide

Property.	Nitrogen.	Carbon Monoxide.
Freezing-point (degrees abs.) .	63	66
Boiling-point (degrees abs.) .	78	83
Critical temperature (degrees abs.)	127	122
Critical pressure (atmos.) . .	33	35
Critical volume (c.cms.) . .	5·17	5·05
Solubility in water (per cent. : 0° C)	2·4	3·5
Density of liquid at boiling-point .	0·796	0·793
Viscosity, $\times 10^6$ at 0° C. . .	166	163

FIGURE XXXVII

STRUCTURE OF N_2, CO AND CN^- (LANGMUIR)

(*J. Amer. Chem. Soc.*, 1919; 41, 903, 1545)



The two nuclei are placed within one octet. The nuclear charges are + 7, + 7 for N_2, + 6, + 6 for CO and + 6, + 7 for the CN^- ion. The extranuclear electrons are arranged in the same way in each of the three cases, and N_2, CO and CN^- are said to be "isosteric."

as in nitrogen *a structure is obtained resembling the chlori* ion, and the compound C_2N_2 is formed analogously to Cl_2, t non-polar union. Rankine has shown, in agreement with th

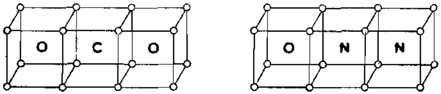
view, that the diameter of the nitrogen molecule does not correspond with two linked neon atoms.[14]

Coming next to carbon dioxide and nitrous oxide, there are 16 disposable sheath electrons in each case, and $E = 16$, $n = 3$, so that $p = 4$, and CO_2 is given the structure shown in Fig. 38, corresponding with $O = C = O$. If N_2O is given the corresponding structure $O = N = N$, the arrangement shown in the second part of the figure is obtained. The differenee again lies in the nuclear charges, which are unsymmetrical in N_2O. The observations of Rankine and Smith are in harmony with these views.[15] Such compounds are known as " isosteres," and have

FIGURE XXXVIII

STRUCTURE OF CO_2 AND N_2O (LANGMUIR)

(*J. Amer. Chem. Soc.*, 1919; 41, 894, 1545)



CO_2 N_2O

Similar structures have been assigned by Langmuir to the gases CO_2 and N_2O, whose physical properties closely resemble each other, the number of sheath electrons being 16 in each case. The structures differ only in the nuclear charges, which are + 8, + 6, + 8 for CO_2 and + 8, + 7, + 7 for N_2O. The ions CNO^- and N_3^- are assigned structures similar to those shown above, the four "comolecules" constituting a group of "isosteres." The nuclear charges are + 6, + 7, + 8 for CNO^-, and + 7, + 7, + 7 for N_3^-.

the same number of sheath electrons arranged in the same way, and differ only in nuclear charges. (The sum of these nuclear charges need not be the same in all isosteres; thus ions can be isosteric with molecules, as well as with one another. Any group of atoms held together by pairs of electrons, whether the group is charged or not, is termed by Langmuir a " comolecule." In this way, nitrogen, carbon monoxide, and the cyanide ion are isosteric comolecules.) It is very probable that the two ions N_3^- and CNO^- are isosteric with each other and with CO_2 and N_2O. If this is correct, the same type of structural arrangement as that shown in Fig. 38 will apply to them. Langmuir does not suppose, however, that when electrons are

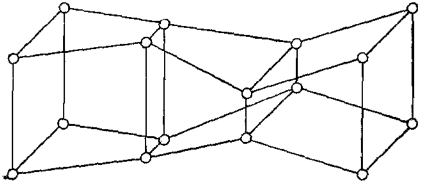
shared the cubic shape of molecule is retained. Thus, Fig. 39 shows Langmuir's space arrangement for carbon dioxide. This will give, in the case of carbon, a tetrahedral arrangement, like that postulated by Lewis for the explanation of triple bonds. It is, perhaps, not very clear why similarly charged electrons should tend to approach each other in this way. The great stability of an electron pair, and the fewness of compounds with odd numbers of sheath electrons are adduced in favour of the view. If two electrons are executing circular motions in the same sense, they may, indeed, attract each other by acting as magnets (section 56).

Nitric oxide is another exceptional case, where there are

FIGURE XXXIX

DIAGRAMMATIC REPRESENTATION OF CO_2 MOLECULE (LANGMUIR)

(*J. Amer. Chem. Soc.*, 1919; 41, 894)



11 sheath electrons. It is suggested that the structure is the same as that given for the nitrogen molecule (Fig. 37) with one additional electron held under restraint in some way within the octet.

The octet structures suggested for certain more normal cases may be now considered, taking as typical examples some ions of the inorganic acids and the complex platinum compounds. The values of E, n and p of Langmuir's equation are tabulated in Table XVII. The values of E are calculated by adding together the number of valency electrons of the constituent atoms or groups, together with $+v$ when v is negative and $-v$ when v is positive, where v is the valency of the ion. Platinum is bivalent in ions 11, 12 and 13, and quadrivalent in

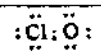
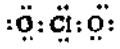
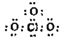
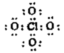
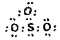
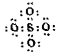
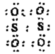
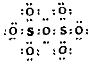
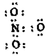
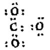
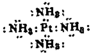
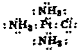
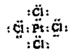
ion 14, so that the sheath electrons are counted as 2 and 4 respectively in these cases. The value of p is calculated from equation (4), by which $p = (8n - E)/2$, except in the case of ion 14. Here, according to Langmuir, the central platinum atom has 6 covalent links, so that there are 12 sheath electrons, and we must substitute for $8n$ in the equation the value $8(n - 1) + 12$.

In a further paper, Langmuir emphasized the importance of isosterism as a basis of similarity and particularly of isomorphism.[16] He gave a list of isosteric comolecules, and showed that in many cases resemblances existed, and that others might reasonably be predicted. Thus, the ions NO_3^{--} and CO_3^{--} were isosteres, and it was known that $NaNO_3$ and $CaCO_3$ were isomorphous. Further, Na^+ and F^- were isosteric and cubic in form, so that they would be expected to pack together in a cubic lattice, which Bragg found to be the case. Again, NaF and MgO would be expected to crystallize in the same way. This was found by Hull.[17] On the other hand, sulphites and carbonates, in spite of the similar appearance of their formulæ, were assigned different constitutions, which accorded with their general divergence in properties, for example, in solubility. Reference to Table XVII will show that the chlorates and sulphites, the perchlorates and sulphates and the nitrates and carbonates should tend to resemble each other in pairs, and this is supported in general by a comparison of their properties. To take a more complicated example, $MnCl_24H_2O$ and $BeNa_2F_4$ show similar crystalline form. Langmuir supposes that the following isosteric atoms and groups replace each other: Be replaces Mn, the 2 Na ions replace the 2 Cl ions and F_4 replaces the 4 water comolecules. These compounds in fact, ionize as follows: $[Mn(OH_2)_4]^{++}$ Cl_2^{--} and $[BeF_4]^{--}$ Na_2^{++}, where $E = 32$, $n = 5$ and $p = 4$ for each. It is clear, however, that a somewhat extended definition of isomorphism will have to be formulated, if such a case is to be included.

Smith has shown, in accordance with the Langmuir theory, that the diameters of the molecules of HBr, H_2Se and H_3As closely approximate to the diameter of the krypton atom.[18]

It has been indicated that the spectrum of ionized potassium exhibits features similar to those of the argon spectrum, and Fowler, using results obtained by Paschen on the spectrum of doubly-ionized aluminium (Al III), has shown that resemblances exist in the spectra of trebly-ionized silicon (Si IV), doubly-ionized aluminium (Al III), singly-ionized magnesium

TABLE XVII.
Structures of Various Ions (Langmuir).

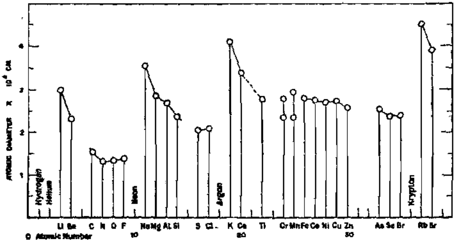
No.	Ion.	E.	n.	p.	Structure.
1	ClO^-	14	2	1	
2	ClO_2^-	20	3	2	
3	ClO_3^-	26	4	3	
4	ClO_4^-	32	5	4	
5	SO_3^{--}	26	4	3	
6	SO_4^{--}	32	5	4	
7	$S_2O_4^{--}$	38	6	5	
8	$S_2O_7^{--}$	56	9	8	
9	NO_3^-	24	4	4	
10	CO_3^{--}	24	4	4	
11	$[Pt(NH_3)_4]^{++}$	32	5	4	
12	$[Pt(NH_3)_3Cl]^+$	32	5	4	
13	$[Pt\,Cl_4]^{--}$	32	5	4	
14	$[Pt\,Cl_6]^{--}$	48	7	6*	

(Mg II) and neutral sodium (Na I).[19] Since these four "atoms" are similarly constituted (differing mainly in nuclear charge), according to static and dynamic theories of atomic constitution, the results are of special interest. Bowen and Millikan, by means of an explosive spark in a vacuum, have succeeded in examining the spectra of atoms denuded of all but one of their valence electrons (e.g., Boron III), in the region between 136 A.U. and 1862 A.U. The spectra of such "stripped" atoms correspond with those of the alkali metals immediately preceding them in atomic number.[19] These results justify the view that

FIGURE XL

CURVE OF ATOMIC DIAMETERS (W. L. BRAGG)

(*Phil. Mag.*, 1920; (vi) 40, 178)



all atomic structures may be referred to those of the inert gases, as the theories of the atom here outlined require.

The Law of Atomic Diameters of W. L. Bragg may also be cited in support of these theories.[20] According to this law, the distance between the centres of two contiguous atoms in a crystal, whether the atoms are alike or not, is equal to the sum of the two individual atomic radii. The periodicity of the atomic diameters is brought out by plotting them against the atomic numbers of the respective elements. The group of alkali metals show the highest peaks on the curve, which is steep on each side of the maxima (see Fig. 40). The atomic diameters are thus periodic functions of the atomic numbers.

That the maxima occur with the alkali metals is in harmony with the view that they mark the beginning of a new shell. On the other hand, the subsequent falling off in diameter until the next member of the group is reached accords very well with the Lewis-Langmuir theory that the electronegative atoms form molecules by sharing electrons, for this effect might cause the spheres of these atoms to have smaller diameters than those of the electropositive elements. Wyckoff, however, has suggested that Bragg's Law is obeyed only in those cases where the atomic environment is not greatly altered by combination.[21]

Langmuir's theory has not unnaturally met with a large amount of criticism. Its merits are mainly of a qualitative kind, and it offers no theory of spectra. Langmuir's attempt to account for spectral series without the assumption of moving electrons cannot be said to possess any real value.[22] Moreover, the series of interpolated elements present difficulties in this theory. Here Bury's theory is of interest.[23] He supposes that the outer shell cannot contain more than 8 electrons, but that building of inner shells can proceed after an exterior shell has been commenced. In this way, the existence of a group of similar transition elements may be explained in a manner somewhat similar to that in Bohr's theory. It appears to be more probable that all the inert gases have outer shells of 8 electrons, or, as in Bohr's theory, 8 electrons in the group of highest total quantum number.

The postulates of the Lewis-Thomson-Langmuir theory are of fundamental importance, and are likely to form the nucleus of future theories of the structures of molecules.

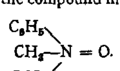
53. Intramolecular Ionization

Brief consideration has already been given to the basis of Thomson's theory of the intramolecular ionization (perhaps "polarization" would be a better term) of some common molecules. Lowry has taken up this question on the basis of the Langmuir theory of the atom in combination.[24] Consider the case of the gases CO_2 and N_2O, whose Langmuir structures are depicted in Fig. 38, on page 227. Counting the net charges on each atom of the two compounds, reckoning an electron which is shared between two atoms as contributing half of its charge to each, the following scheme is obtained :—

	Carbon Dioxide.			Nitrous Oxide.		
	:Ö:	:C:	:Ö:	:Ö:	:N:	:N̈:
Nuclear charge .	+8	+6	+8	+8	+7	+7
"Helium" electrons	−2	−2	−2	−2	−2	−2
Shared electrons .	−2	−4	−2	−2	−4	−2
Other electrons .	−4	0	−4	−4	0	−4
Net charge .	0	0	0	0	+1	−1

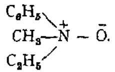
It appears from this that if carbon dioxide is written $O = C = O$, nitrous oxide should be distinguished in some way, such as by $O = \overset{+}{N} = \overset{-}{N}$ or $O = N \stackrel{\rightharpoonup}{=} N$ (where the barb denotes an electrovalency directed from the central nitrogen atom to the outer nitrogen atom) in spite of the physical similarity of the two gases. The central nitrogen atom contributes both electrons to the bond, and has lost a half share in two electrons, which has been gained by the outer atom. The central atom, therefore, has one positive charge in excess, and the outer atom one negative charge in excess. A "mixed" bond, consisting of one electrovalency (due to the opposed charges) and one covalency (due to the shared electrons), is formed, without in any way disturbing the conception of octet arrangement on which the theory of "primary" valency is based.

Oxygen has 6 electrons in its shell, so that it requires 2 electrons to complete its octet, and an oxygen atom can attach itself to any already saturated octet, so long as that octet is not already surrounded by four other atoms or radicals. The latter octet will contribute both shared electrons, and a mixed bond will result, and thus an atom can exert two additional valencies. Now, methane cannot be converted into an oxide. This must be attributed to the fact that all the electrons of the carbon of methane are already shared. The case is quite different, however, with compounds of the ammonia type. Thus Meisenheimer prepared the compound methylethylaniline oxide:

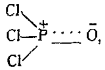


In the trisubstituted ammonia, one free edge of the nitrogen octet remains, which is gripped by the oxygen atom in the above compound. The new bond is formed by electrons which are both contributed by the nitrogen atom. A mixed bond is

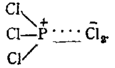
formed, the nitrogen acquiring a positive, and the oxygen a negative, charge. It thus happens that nitrogen can raise its valency from 3 to 5 by taking up two new bonds, one of electrovalency and the other of covalency. The new compound may, therefore, be written—



Prideaux has applied Lowry's principle to the compounds $POCl_3$ and PCl_5.[25] The former is written—



where the phosphorus atom supplies both electrons for the bond. Similarly, phosphorus pentachloride is given the structure—

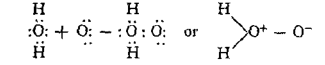


This Cl_2 group must be attached by the two octets sharing one electron each with the phosphorus atom, and a single negative charge is distributed between them. The question of two octets sharing one electron only has been considered by Thomson in connection with the possible compound NCl_5.[26] Prideaux suggests that such a Cl_2 group can be replaced by oxygen, and that it is only when chlorine is attached by a pure electrovalency that it can be replaced by hydroxyl. Another useful suggestion is made, that bonds should be labelled to show from which of two atoms the electrons are derived. The following illustrates the method:—

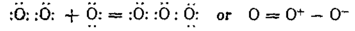
Iodine chloride.	Iodine trichloride.
Cl — I,	Cl — $\overset{+}{\text{I}}$ ···· $\overset{-}{\text{Cl}}_2$,
or, Cl S I.	or, Cl S I :) Cl_2.

The sign S indicates that each atom has contributed one electron to the link, and the sign :) that both electrons come from the atom with which they are bracketed.

Lowry further suggested that ozone and hydrogen peroxide should be given formulæ containing mixed bonds, where an oxygen atom is tacked on to a water molecule and an oxygen molecule respectively, so that the central oxygen atom in each case raises its valency by 2 units :—



Hydrogen Peroxide.



Ozone.

These principles are also applied to explain the varying stability of the negative ions of the oxy-acids of chlorine, sulphur, phosphorus and silicon. Table XVIII shows a number of such cases, the mixed bond being represented for convenience by a single bar.

This table is worthy of special consideration. The ion Cl^- has a completed octet, and can share 2, 4, 6, or 8 electrons, with 1, 2, 3, or 4 oxygen atoms, if it contributes both electrons for every bond. As each pair of electrons becomes appropriated, the chlorine ion loses a half share in 2 electrons, equivalent to the loss of 1 negative charge. Thus the Cl atom in ClO^- is uncharged, while in ClO_2^-, ClO_3^-, and ClO_4^- it carries 1, 2 and 3 positive charges respectively, the net charge being -1 in each case, as demanded by the single valency. Similarly, the ion S^{--} has a completed octet, and might be expected to behave in a similar way. In this way, the hypothetical ions SO^{--} and SO_2^{--} would carry charges of -1 and 0 respectively on the sulphur atom, and the ions SO_3^{--} and SO_4^{--} charges of $+1$ and $+2$. The same argument requires that phosphorus should be P^+ in PO_4^{---}, and that silicon in SiO_4^{----} should be uncharged. Now, as the growth of positive charge on the central chlorine atom of the series of acids proceeds, an increase in stability might be expected, which is actually observed. Moreover, it is not surprising that the ions SO^{--} and SO_2^{--} should be non-existent, since there is no positive charge to hold the negative oxygens together. It appears, however, that in certain cases an uncharged central atom can hold negative oxygens with a certain degree of stability, as in ClO^-, PO_3^{---}

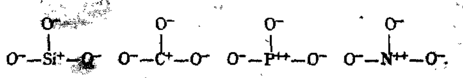
TABLE XVIII

Structures of Negative Ions of Some Oxy-Acids Showing Mixed Bonds

Hypochlorite ion . .	ClO^-	$Cl - O^-$
Chlorite ion	ClO_2^-	$O^- - Cl^+ - O^-$
Chlorate ion	ClO_3^-	$O^- - Cl^{++}(-O^-) - O^-$
Perchlorate ion . . .	ClO_4^-	$O^- - Cl^{+++}(-O^-)_2 - O^-$
Ion SO^{--} (unknown) .		$S^- - O^-$
Ion SO_2^{--} (unknown) .		$O^- - S - O^-$
Sulphite ion	SO_3^{--}	$O^- - S^+(-O^-) - O^-$
Sulphate ion	SO_4^{--}	$O^- - S^{++}(-O^-)_2 - O^-$
Phosphate ion . . .	PO_4^{---}	$O^- - P^+(-O^-)_2 - O^-$
Silicate ion	SiO_4^{----}	$O^- - Si(-O^-)_2 - O^-$

and SiO_4^{----}, though an ion such as SO^{--}, where both charges are negative, cannot possibly exist.

With regard to the ions of the dehydrated acids H_2SiO_3, H_2CO_3, HPO_3 and HNO_3, Lowry gives the central atom of each ion a depleted octet, or "sextet." This makes the arrangements of the four ions symmetrical :—



This is not in accordance with the view of Langmuir, who has given one atom of oxygen in each case a double bond (see ions 9 and 10 of Table XVII). The view here presented is held to be more in line with the crystallographic data, by which, for example, the three oxygen atoms of the CO_3^{--} ion of calcite are in one plane, and symmetrically placed with regard to the carbon atom, and in the same plane with it. The same is true of $NaNO_3$, but not of $Pb(NO_3)_2$, so that no very universal rule can be given. With the ClO_3^- ion, however, the crystallographic evidence shows that the three oxygen atoms are not in the same plane as the chlorine atom, so that Lowry concludes that this supports the theory of a tetrahedral arrangement of four duplets of "M" electrons.[27]

The suggestion that the innermost, or K electrons may be utilized to build up an extended octet of larger size, is due to Eastman.[28] By this means, a structure for the compound B_2H_6, which is rather a stumbling block for the octet theory, is proposed. Thus Robinson supposes that the inner duplet from one of the boron atoms is brought into play to provide the connecting valency bond and to complete the octets, so that this compound may be written $H_3B : BH_3e_2$, where e_2 represents the helium duplet not called out.[29] This involves, following Lowry, that opposite charges should reside on the two boron atoms, which are connected by a mixed bond: $H_3\overset{+}{B} - \overset{-}{B}H_3$. This formula is analogous to that proposed by Lowry for ethylene in its reactive condition: $H_2\overset{+}{C} - \overset{-}{C}H_2$. It has been shown by Stewart and Edlund that the union of ethylene with bromine is a surface reaction, which suggests that ordinary ethylene must be activated by contact catalysis before it can react in this case.[30] Further, Norrish has shown that the surface is not capable of causing the activation of the dry gases if it is composed of a non-polar substance such as paraffin wax.[31] On the other hand, polar substances, such as glass or stearic acid, form catalytically reactive surfaces. Thus Lowry's theory of the nature of the double bond in an activated form of ethylene derives considerable support. It is not quite so easy, however, to accept a similar formula for boroethane, which reacts with chlorine to give a substitution product B_2H_5Cl, and not an addition product as ethylene does.[32] Lowry has applied the theory of mixed double bonds to explain a number of phenomena familiar more particularly to organic chemists.[33]

Objections have been raised against the theory of intramolecular ionization. Thus, for instance, the compound magnesium methyl iodide is formed, according to the octet theory, by the iodine atom and the methyl group taking an electron each from the magnesium atom to complete their octet systems, so that it may be represented by the formula $H_3\overset{-}{C}.\overset{++}{Mg}.\overset{-}{I}$. It is found that the compound, however, gives non-conducting solutions. This objection may be met by supposing that a suitable ionizing solvent has not been found. Again, it has been pointed out that the theory is in conflict with Langmuir's third postulate. As Langmuir himself, however, has admitted many exceptions to this postulate, the objection appears to have no serious weight. A more serious point appeared to have been raised by Sugden, somewhat as follows.[84] In order to explain the facts of stereochemistry, it is necessary to postulate free rotation about a covalent linkage. If this is admitted, then it would appear that Lowry's formula for ethylene must also give free rotation, which is opposed to the stereochemical models of van't Hoff, by which the existence of geometrical isomerides (cis and trans forms) is explained on the ground of a lack of such rotation about a double bond. In reply, Lowry pointed out that, in the case of ethylene, the mixed bond formula represented the active state of the compound, so that ordinary stereochemical considerations might still apply to the " dog curled up and resting," i.e. the non-reactive condition. Another interesting point was raised in connection with pure stereochemical theory. In the case of the symmetrical derivatives of diphenyl, $C_6H_5 \cdot C_6H_5$, where the classical theory predicts that stereoisomerism and optical activity should be absent, both of the latter phenomena have been detected. Lowry remarks that " the subject is now ' open to discussion ' on the broadest possible lines, including those suggested by the electronic theory of valency." [85]

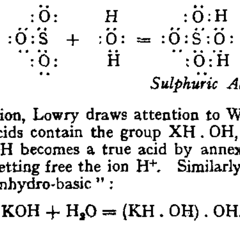
54. Theories of Acidity and of Alternating Polarities

Reference has been made to Kossel's theory of acid and basic substances, which depends on the volumes and charges of ions (p. 218 *seq.*). Kossel gives the following series as showing that as the number of positive charges (on the parts of the molecules shown below outside their respective brackets) increases, the binding towards oxygen increases, so that the binding towards hydrogen diminishes, with corresponding tendency of

the latter to split off as an ion. There is thus a gradual development of acidity in passing along the series from left to right:

NaOH	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClO_2(OH)$
+ 1	+ 2	+ 3	+ 4	+ 5	+ 6	+ 7

In Langmuir's theory, acids are regarded as substances whose molecules readily detach hydrogen ions (hydrogen nuclei). Similarly, bases are substances whose molecules readily take up hydrogen ions. Lewis has recently given a more general definition as follows: "An acid is a substance which gives off the cation or combines with the anion of a solvent; a base is a substance which gives off the anion or combines with the cation of a solvent." This definition applies to non-aqueous solutions: thus KNH_2 is a base in liquid ammonia, and KCl is a base in liquid hydrochloric acid. A definition based on electron theories is the following: "A basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom; an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms."[38] Thus the "lone pair" of electrons in NH_3 can take up an H^+ and form the ion NH_4^+. The anhydride SO_3 takes up a lone pair of electrons from a water molecule in forming sulphuric acid:



Sulphuric Acid.

In this connection, Lowry draws attention to Werner's theory, by which all acids contain the group XH . OH, and the "anhydro-acid" XH becomes a true acid by annexing OH^- from water, and so setting free the ion H^+. Similarly, even KOH is regarded as "anhydro-basic":

$$KOH + H_2O = (KH . OH) . OH.$$

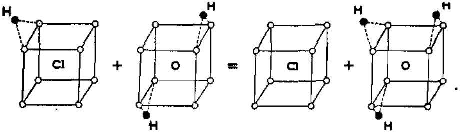
In hydrochloric acid, the hydrogen nucleus shares a pair of electrons with the chlorine atom, and anhydrous liquid HCl is a non-conductor. In contact with water, however, the hydrogen nucleus attached to the chlorine octet becomes tacked on to the water octet, setting free the ion Cl^-. If the oxygen nucleus of water (nuclear charge + 8) repels the hydrogen ion less than

the chlorine nucleus (nuclear charge + 17) transference will occur, as shown in Fig. 41. The change may be represented

Figure XLI

IONIZATION OF HYDROCHLORIC ACID

(See *Chem. and Ind.*, 1923; 42, 46, 1049)



in symbols thus:—

$$:\underset{\cdot\cdot}{\ddot{Cl}}:H + H:\underset{\cdot\cdot}{\ddot{O}}:H = :\underset{\cdot\cdot}{\ddot{Cl}}: + H:\underset{\ddot{H}}{\ddot{O}}:H$$

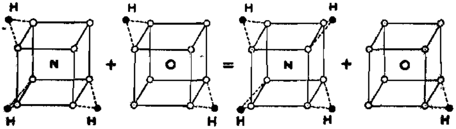
that is,

$$HCl + H_2O = Cl^- + OH_3^+.$$

Figure XLII

IONIZATION OF AMMONIA

(See *Chem. and Ind.*, 1923; 42, 46)



In the case of ammonia, the repulsive force due to the nitrogen nucleus (charge + 7) is smaller than that due to the oxygen nucleus of the water, so that transference of a hydrogen nucleus occurs from the water to the nitrogen octet, as represented in Fig. 42, or, in symbols,

$$NH_3 + H_2O = NH_4^+ + OH^-.$$

The weak basicity of ammonia must be attributed to the small proportion of hydrogen ions attracted in this way. If NH_4OH is formed, it would be expected to be ionized completely at once. Support may be found for the view that this substance is not involved in the ionic equilibria, and the existence of its molecules is questioned by Caven.[87]

In the case of methane, CH_4, the small nuclear charge of the carbon (+ 6) might tend to attract hydrogen nuclei, but the octet is already complete. Thus methane behaves neither as an acid nor as a base.

It is well known that the halogen-substituted acids of acetic acid are much stronger than acetic acid itself, but that if the length of intervening chain is increased, the acidity diminishes. This appears to suggest some mechanism (transmitted along the chain and set in motion by the substituent halogen) which increases the repulsion on the hydrogen ion.

Table XIX shows the values of the dissociation constants of a few straight chain organic acids, together with those of some chlor-substituted derivatives.

TABLE XIX

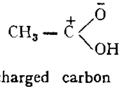
Dissociation Constants of Halogenated Acids at 25° C.

Acids.	Formula.	Dissociation Constant. ($\times 10^5$).
Acetic	CH_3COOH	1·8
Monochloracetic	$CH_2ClCOOH$	155
Dichloracetic	$CHCl_2COOH$	5000
Trichloracetic	CCl_3COOH	30000
Propionic	CH_3CH_2COOH	1·4
α-chlorpropionic	$CH_3CHClCOOH$	147
β-chlorpropionic	CH_2ClCH_2COOH	8·6
Butyric	$CH_3CH_2CH_2COOH$	1·5
α-chlorbutyric	$CH_3CH_2CHClCOOH$	139
β-chlorbutyric	$CH_3CHClCH_2COOH$	8·9
γ-chlorbutyric	$CH_2ClCH_2CH_2COOH$	3·0

It is clear that the position and number of chlorine atoms are the factors which determine the relative acidities of the substances considered. The effect of increasing the number of chlorine atoms is shown by the dissociation constants of the substituted acetic acids, and the effect of increasing the length of chain between the halogen and the ionizable hydrogen is

shown by the α- and β-chlorpropionic and the α-, β- and γ-chlorbutyric acids.

The mechanism by which the halogen exerts its effect appears to be a displacement of the nuclei relatively to the shells of electrons, by the repulsive force of the chlorine nucleus. In the case of acetic acid, Lowry suggests an internally-polarized formula, the central carbon atom bearing a positive charge :—



Here the positively-charged carbon transmits through the hydroxylic oxygen a repulsion just sufficient to enable the terminal hydrogen nucleus to escape as an ion. The repulsive effect of the carbonyl oxygen nucleus is counteracted by the negative charge.[84] Substitution of the hydrogen of a methyl group by chlorine presumably increases the positivity of the carbon attached to hydroxyl, and thus increases the repulsive force on the relatively light hydrogen nucleus. Similarly, the acidity of the substances in the following series increases from the first onwards: $HClO$, $HClO_2$, $HClO_3$, $HClO_4$. Reference to Table XVIII on page 236 will show that the positive charge on the central chlorine atom increases in the same order, and thus increasing stability is accompanied by increasing acidity. The acidity of the following series increases in a similar way: H_4SiO_4, H_3PO_4, H_2SO_4, $HClO_4$. This may again be associated with the increasing charge on the central atoms of the molecules.

At this point it is convenient to discuss the ways in which, according to recent theories, chemical affinity is transmitted in chains. Two kinds of mechanism may be distinguished.[88] The first is termed the "general" effect, which is the mechanism considered above, by which an atom exerts an effect which diminishes as the distance increases. The other is the effect of "alternate induced polarities," in which alternate atoms are affected in different ways. Organic chemists have long recognized the existence of properties which alternate along a chain. Flürscheim first suggested that a substituent might cause the distribution of electric force to alternate.[89] Substituent groups may be divided into "acylous" groups, which increase acidity, and "basylous" groups which decrease it. The theory of alternate induced polarities is developed from an electronic point of view both by Lapworth and by Kermack and Robinson.

Lapworth considers the modes in which valencies are readjusted when a " constraint " is set up at one point of a molecule by a " key " atom, and propagated to other parts of the molecule.[40] In terms of the electronic theory of valency, this propagation consists simply in the movement of electrons from one shared position to another. Key atoms which cause such constraints are those of oxygen, nitrogen and chlorine. These atoms have a greater tendency to adhere to their electrons than carbon has to its electrons. This leads, according to Lapworth, to the principle of alternate induced polarities, whereby molecules in their reactive condition have atoms oppositely polarized along a chain, being alternately positively and negatively charged. In Flürscheim's theory, however, the amount of residual affinity of the atoms of a chain is supposed to alternate, no assumption being made in regard to polarity.

Kermack and Robinson call attention to the fact that the introduction of electronegative atoms, such as oxygen, nitrogen and chlorine into a molecule increases the power of the whole assemblage to retain electrons, as in the substituted acetic acids.[41] The retention of the negative electron of hydrogen is facilitated by the presence of halogen in a molecule, with consequent increase of dissociation constant and of acidity. These negative atoms tend to attract electrons and make up a stable octet. Thus, considering the system—

$$:\ddot{\underset{\cdot\cdot}{A}}:\ddot{\underset{\cdot\cdot}{B}}:\ddot{\underset{\cdot\cdot}{C}}:\ddot{\underset{\cdot\cdot}{D}}:$$

if the octet surrounding A tends to become stable, a partial appropriation by A of the electrons shared with B occurs. This tends to make the octet surrounding B unstable, for it is supposed that a partially disintegrated octet tends towards further disruption. In these circumstances, the atom C has no difficulty in appropriating two electrons from B, and in so doing may form a stable octet, which renders D unstable, and so on. The atoms A, B, C, D . . . become in this way alternately negative and positive, according as they tend to take up or to give up duplets shared with neighbouring atoms. Thus, in allyl chloride the polar condition represented by—

$$\overset{-}{Cl} . \overset{+}{C}H_2 . \overset{-}{C}H : \overset{+}{C}H_2$$

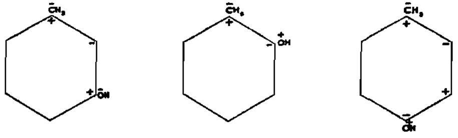
is assigned, so that with $\overset{+-}{HBr}$, the product formed is—

$$Cl . CH_2 . CH_2 . CH_2Br.$$

Similarly, the hydrolysis of $CH_3 . \overset{+}{C}O . \overset{-}{N}H_2$ by $H\overset{-}{O} . \overset{+}{H}$ yields CH_3COOH and NH_3. In these cases, unlike charges attract each other, and NH_2 behaves apparently as an acylous group.

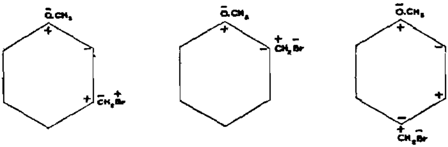
Experience has shown that the alternating effect is transmitted more easily when unsaturated linkages occur in a chain. This is attributed to the fact that when, for example, four electrons are shared in the formation of a double bond, these electrons induce greater constraint on the octets of which they form part and possess consequently increased mobility. The theory is applied to the conjugation of organic compounds.

In agreement with the theory of alternate induced polarities, meta-cresol appears to have a higher ionization constant than ortho- or para-cresol. This is to be anticipated if the hydrogen of the methyl group acts positively, producing the induced arrangement shown below :—



m-cresol o-cresol p-cresol

The alternation of polarities in these cases gives the oxygen of the hydroxyl group a positive charge in the ortho and para positions and a negative charge in the meta position. The hydrogen nucleus experiences greater tendency to split off as an ion when attached to negative oxygen, which tends to hold the duplet between itself and hydrogen, than when the charge on the oxygen is positive, in harmony with observation. Further, Lapworth and Shoesmith have drawn attention to an interesting case in connection with the three isomerides of methoxybenzylbromide. It is shown that the meta compound is the least easily hydrolyzed, but the most readily reduced by hydrogen iodide. The theory of alternating polarities gives the following scheme:—



(1) meta — (2) ortho — (3) para —
methoxybenzylbromide

Here the oxygen of the substituent group O . CH_3 acts as a negative key atom. This makes the bromine atom positive in the meta compound and negative in the other cases. When the bromine atom is positively charged, there is little tendency for it to unite with the positive hydrogen of $\overset{+}{H}.\overset{-}{O}H$ to give HBr, and thus the meta compound is the least readily hydrolyzed. On the other hand, the carbon atom of the CH_2 group is charged negatively in the meta compound and positively in the other cases, so that in the former case there is greater tendency to unite with the positively-charged hydrogen of $\overset{+\,-}{HI}$, with consequent reduction than in the latter cases. Thus theory and experiment are brought into line.

The advantage of comparing isomerides in this way is that general polar effects are eliminated. In general, however, such effects are of considerable importance. It is found, for example, *that (independent of the position of a substituent group) the* more electropositive the molecule is, the quicker is hydrolysis brought about.

Henstock has introduced a development, in which, following Langmuir, he regards the atomic nucleus as a dipolar sphere, and considers the tubes of force within the atom.[63] He arrives at a system of labelled bonds which show alternating polarities. Thus, ammonia and certain derivatives are written as follows :—

$$\begin{array}{c} H\overset{+\,-}{—}N\overset{-\,+}{—}H \\ |^{-}_{+} \\ H \end{array} \quad \begin{array}{c} H\overset{+\,-}{—}N\overset{-\,+}{—}H \\ |^{+}_{-} \\ Cl \end{array} \quad \begin{array}{c} Cl\overset{-\,+}{—}N\overset{+\,-}{—}Cl \\ |^{+}_{-} \\ Cl \end{array} \quad \begin{array}{c} H\overset{+\,-}{—}N\overset{-\,+}{—}H \\ |^{+}_{-} \\ CH_3 \end{array} \quad \begin{array}{c} CH_3\overset{-\,+}{—}N\overset{+\,-}{—}CH_3 \\ |^{+}_{-} \\ CH_3 \end{array}$$

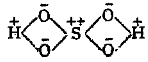
The theories of acids and bases reviewed in this section show general qualitative agreement with experiment. It may be

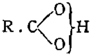
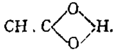
hoped that some account of a more quantitative description may materialize, where the strengths of linkages in different compounds in relation to each other are considered. The views of Kossel, given earlier, perhaps provide some basis for such discussion.

55. Co-ordination Compounds

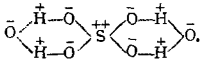
The conception of residual affinity was used by Werner to explain cases where atoms appeared to exert more than their normal number of valencies. In the light of the electronic theory of valency, however, no such assumption is necessary, and co-ordination compounds may be explained by the single hypothesis of the covalent linkage, already introduced for simpler types of compounds. Any considerations tending to reduce the number of fundamental postulates simplify the general treatment of chemical combination, and are valuable if they are tenable. Co-ordination has received a large amount of attention in recent papers, the more important of which will now be reviewed.

It is convenient to commence with the case of hydrogen. This element, being the generally accepted " valency standard," appears in the text-book definition of equivalent weight. Hydrogen is implicitly supposed to possess only one valency bond, and is, therefore, incapable of joining two atoms together. Lowry and Burgess, however, have devoted a paper to the evidence that this conception is false.[44] The simplest chemical evidence for the view that hydrogen can be divalent is afforded by the existence of the ion FHF^-, formed from potassium hydrofluoride, KHF_2. The 16 sheath electrons complete the octets of the two fluorine atoms in this ion, leaving the hydrogen nucleus to link the octets together. The ion may, therefore, be represented thus : $:\ddot{\underset{..}{F}}:H:\ddot{\underset{..}{F}}:$. A similar explanation of the association of liquid water is given by Latimer and Rodebush.[45] The theory of mixed double bonds has already introduced an element of symmetry into the various ions shown in Table XVIII on page 236. Similarly, sulphuric acid may be formulated as follows :—



which accords very well with the views of Werner and of Hantzsch.[46] In the case of the carboxylic acids, the latter suggests that two forms may be possible, one unsymmetrical and not ionizable, from which the esters are derived, and another symmetrical and ionizable from which the salts are derived. These may be represented by R . CO . OH and by  respectively. Lowry's symmetrical formula for acetic acid shows a closed ring, thus:  This differs from Hantzsch's structure only in that the hydrogen atom is not placed outside the sphere of co-ordination, but serves as a connecting link between the two oxygen atoms.

Returning for a moment to the formula given above for sulphuric acid, it is clear that instead of two hydrogen atoms attached to the four oxygens, two water molecules might be tacked on to the " homopolar " ion as follows :—



It is an essential part of Lowry's theory that the competition between water molecules and hydrogen nuclei for homopolar ions may be an important factor in determining the strength of acids. Morgan and Main Smith have shown that a hydrogen ion and a water molecule are sometimes mutually replaceable in co-ordination complexes.[47]

Before proceeding to electronic theories of co-ordination compounds of more complex type, the older theories of " free " and of " supplementary " (residual) valencies, the development of which was so largely due to Werner, will be considered. Free positive and negative valencies were characteristic of atoms and radicals, while supplementary valencies were shown by molecules. Thus, in the case of a molecule of potassium fluoride, the free positive valency of potassium was not quite neutralized by the free negative valency of fluorine, so that the molecule possessed a small positive residual affinity. By a similar argument, a molecule of hydrogen fluoride was supposed to possess a small negative residual affinity. Combination was,

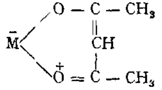
therefore, possible between molecules by virtue of their residual affinities, giving potassium hydrofluoride, KF . . . HF, the dotted line representing the residual valency bond. Similarly, according to Werner's theory, the residual affinities of sulphur trioxide and water molecules were responsible for combination with the formation of sulphuric acid, represented by

$$\begin{array}{l} \quad O \\ \quad \| \\ O = S \; . \; . \; . \; (OH_2). \\ \quad \| \\ \quad O \end{array}$$

Subsequent rearrangement resulted in the formation of a complex radical SO_4, thus: $(SO_4)H_2$. The hydrogen was supposed to be outside the sphere of the complex radical, and was, therefore, readily split off in ionic form. In a similar way, hydrogen platinichloride was written $H_2(PtCl_6)$, and the complex cobaltammines given formulæ of the type $[Co(NH_3)_6]Cl_3$, in each of which cases the "co-ordination number" was 6. On this basis, Werner was remarkably successful in explaining the observed isomerism of complex co-ordinated compounds. The valency of the group containing the co-ordinated ammonia or water molecules was also explained. Thus in the group $[PtCl_2(NH_3)_4]$, the valency of the platinum $(+ 4)$ was partly neutralized by the valency of the two chlorine atoms $(- 2)$, so that a net valency of $+ 2$ remained, enabling the following compound to exist: $[PtCl_2(NH_3)_4]Cl_2$, where two only of the four chlorine atoms were split off in ionization. Similarly, in the following case, the valency of platinum $(+ 4)$ was neutralized by the negative valency of five chlorine atoms $(- 5)$, so that the net valency of the complex group was negative, and equal to $- 1$: $[Pt(NH_3)Cl_5]K$.

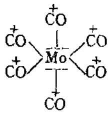
Returning to considerations based on theories of atomic structure, after helium in the periodic table, there are two series of eight elements, where Langmuir's theory might lead to the supposition that a greater covalency than four is not possible, since the sharing of electrons is limited to four edges of a cube. This appears to be confirmed by experiment as far as the end of the first of the two series, but not for the elements between neon and argon of the second series. For instance, sulphur forms a non-polar and inert hexafluoride SF_6, which seems to involve 6 covalent linkages on the sulphur. Similarly, silicon forms an ion, SiF_6^{--}. Again, aluminium and silicon form compounds AlA_3 and $(SiA_3)Cl$, where A represents the acetylacetone group.

When written in ring form, this group is seen to require two covalent linkages for each equivalent of metal linked with it :—



The oxygen atom marked $\overset{+}{O}$ contributes both electrons for the link with the metal, so that it must be regarded as positively charged, and the metal negatively charged.[48] The co-ordination numbers of aluminium and silicon are, therefore, equal to 6 in their acetylacetone compounds, involving 6 covalencies. It is noteworthy that boron does not exert a greater co-ordination number than 4 in its corresponding compound : $(BA_2)Cl$. The rule which appears to limit the maximum co-ordination number of an atom is given on page .

In the longer series of elements, higher covalencies are possible. For instance, zirconium in the second series of 18 elements gives an acetylacetone compound ZrA_4. Other examples are provided by the carbonyls of iron and molybdenum: $Fe(CO)_5$ and $Mo(CO)_6$. In the latter case, molybdenum with 6 sheath electrons shares 12 further electrons with the 6 carbonyl groups, and exerts a covalency of 6. By this means, the number of sheath electrons (shared or otherwise) is made up to 18, which is the number in the outer shell of the next inert gas, xenon. Further, since the carbonyl groups contribute both electrons for their linkages, the carbonyl groups develop positive charges and the molybdenum atom six negative charges, so that the compound should be written, following Lowry,



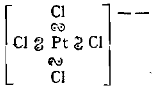
where six mixed bonds are developed.

It is noticeable that the elements of triad groups, in the middle of the long series, show a special tendency to form complex co-ordinated compounds. It is, moreover, in the

eighth group of the periodic table of Mendeleeff that, according to Bohr, sub-groups of 6 each are being built up, and in this part of the table sixfold symmetry and a maximum Werner co-ordination number of 6 are found.[40]

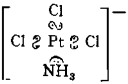
Consider, again, the case of the complex platinum compounds formed by co-ordinating molecules of water or ammonia. Platinum has 78 extranuclear electrons, which Langmuir arranges in shells according to the following scheme from the nucleus outwards: 2, 8, 8, 18, 18 and 24. Bohr's arrangement, according to total quantum numbers, is different: 2, 8, 18, 32 and 18. This last group of 18 electrons, which consists of three sub-groups of 6 electrons each, having orbits represented by 5_1, 5_2 and 5_3, is just completed with platinum. The element forms two main series of compounds, in which its co ordination numbers are 4 and 6. These series may be derived from the two compounds represented by K_2PtCl_4 and K_2PtCl_6.

Considering the platino-series, the ions of potassium platinochloride are $2K^+$ and $PtCl_4^{--}$. The negative ion may be formulated as shown below by the platinum atom forming covalent links with the four chlorine atoms. It may be supposed that each chlorine atom gives one electron for the two shared electrons, the other coming from the platinum. The ion may be written as follows, using the method explained on page 234:—

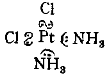


In this way, the central atom is concerned with four additional electrons from four chlorine atoms, as well as two further electrons from two potassium atoms gained in forming the ion, so that its "effective" atomic number is increased to $78 + (4 + 2) = 84$. The latter term is defined by Sidgwick as the number of electrons (shared or not) attached to an atom in question. The chlorine atoms in the above ion can be replaced, one by one, by molecules of water or ammonia. A little consideration will show that, if substitution occurs, since the octets of water and ammonia are complete, the substituent molecule must contribute both electrons for the link. Using the suggested method of designation, (: H_2O or (: NH_3 replaces

ʒ Cl. An electron is evidently expelled during the process, so that the new ion has a negative valency of one unit less, that is, of $2 - 1 = 1$. This may be expressed in the following way, where an ammonia molecule has replaced a chlorine atom :—



This ion forms part of the compound $K[(NH_3)PtCl_3]$. Further substitution expels another electron, and the new complex is a non-electrolyte :—



Following out this scheme, replacement of the two remaining chlorine atoms gives rise to *positively* charged ion complexes, so that compounds of the type $[(NH_3)_3PtCl]Cl$ and $[(NH_3)_4Pt]Cl_2$ are obtained, where positive valencies of one and two respectively occur. In the former case, one atom of chlorine is split off in ionization, and, in the latter, two atoms are split off. This explanation, it will be observed, is independent of any hypothesis of residual affinity.

Similar explanations apply to the platini-series, and to the complex compounds of the same type formed by other elements. It is convenient to have a ready method of calculating the effective atomic number in any given case. Following Sidgwick, this may be derived by means of the relation—

$$z = Z + a + 2b + c \quad . \quad . \quad (5)$$

where Z is Moseley's atomic number,

a is the number of links where *one* electron is supplied by another atom or group, e.g., by Cl, CN, NO_2, $\frac{1}{2}C_2O_4$, etc.,

b is the number of links where *two* electrons are supplied by another atom, e.g., atoms of the groups NH_3, H_2O,

c is the number of electrons *added* by ionization.

It will be clear that *z* is positive when the atom considered forms part of a negative ion, since in this case it *receives c* electrons

from its positive partner, and, on the other hand, that *c* is negative when the atom forms part of a positive ion. To show how this rule works, values are given in Table XX of *z*, the effective atomic number, for the five platino-compounds mentioned above, as well as for the corresponding series of platini-compounds, together with the values of *Z*, *a*, 2*b* and *c*.

TABLE XX

Effective Atomic Numbers of Complex Platinum Compounds

Formula of Compound.	Z.	a.	2b.	c.	z.
I. Platino-Series; Co-ordination Number = 4.					
1. $K_2(PtCl_4)$	78	4	0	+2	84
2. $K(NH_3 . PtCl_3)$	78	3	2	+1	84
3. $(NH_3)_2PtCl_2$	78	2	4	0	84
4. $[(NH_3)_3PtCl]Cl$	78	1	6	−1	84
5. $[(NH_3)_4Pt]Cl_2$	78	0	8	−2	84
II. Platini-Series; Co-ordination Number = 6.					
1. $K_2(PtCl_6)$	78	6	0	+2	86
2. $K(NH_3 . PtCl_5)$	78	5	2	−1	86
3. $(NH_3)_2PtCl_4$	78	4	4	0	86
4. $[(NH_3)_3PtCl_3]Cl$	78	3	6	−1	86
5. $[(NH_3)_4PtCl_2]Cl_2$	78	2	8	−2	86
6. $[(NH_3)_5PtCl]Cl_3$	78	1	10	−3	86
7. $[(NH_3)_6Pt]Cl$	78	0	12	−4	86

For each series, the co-ordination number is given by $(a + b)$. The effective atomic number is constant in each series, and, in the case of the second series, is equal to the atomic number of the following inert gas niton. That this is a fairly general tendency has been emphasized by Spiers[50] and Brockman.[51] Greater conformity with the rule is obtained if it is possible to utilize the two inner (K) electrons. Lowry wisely calls this robbery good algebra but bad physics, pointing out the extreme tenacity with which the inner electrons are held, particularly in heavy atoms, as is evidenced by their ionization potential.[27] The case of the hydrides of boron, where Eastman's suggestion has proved useful, is different, in that the K electrons which are shared are not necessarily supposed to be brought to the surface of the atom.

Sidgwick has calculated the effective atomic numbers of various atoms in complex co-ordinated compounds, and has obtained the number of electrons (given in column headed "*y*" in Table XXI) in the outermost Bohr orbits by subtracting the number of electrons in lower quantum groups (given in column

headed " x " in same Table).[49] This number is $2 + 8 = 10$ for the iron-cobalt-nickel series, $2 + 8 + 18 = 28$ for the ruthenium-rhodium-palladium series, and $2 + 8 + 18 + 32 = 60$ for the osmium-iridium-platinum series. In Table XXI, the co-ordination number of the atom is shown in Roman numerals, and the divalent radicals are denoted by asterisks. The symbols En and Dip refer to the ethylene diamine and dipyridyl molecules respectively.

TABLE XXI

Outermost Orbital Electrons of Atoms in Co-ordinated Complexes

	Formula of Compound.		Z.	a.	$2b$.	c.	z.	x.	y.
1.	$(En_3{}^*Cr)Cl_3$	Cr(VI)	24	0	12	−3	33	10	23
2.	$(Dip_3{}^*Fe)Cl_2$	Fe(VI)	26	0	12	−2	36	10	26
3.	$[(NH_3)_5Co(NO_2)]Cl_2$	Co(VI)	27	1	10	−2	36	10	26
4.	$[H_2O)(NH_3)_5Rh]Cl_3$	Rh(VI)	45	0	12	−3	54	28	26
5.	$(PdCl_4)K_2$	Pd(IV)	46	4	0	+2	52	28	24
6.	$[(C_2O_4)_2{}^*(OH)_2Ir]K_3$	Ir(VI)	77	6	0	+3	86	60	26
7.	$(PtCl_6)K_2$	Pt(VI)	78	6	0	+2	86	60	26
8.	$(NH_3)_2Pt\ Cl_2$	Pt(IV)	78	2	4	0	84	60	24
9.	$(AuCl_4)K$	Au(IV)	79	4	0	+1	84	60	24

It appears from this table that a tendency exists in atoms xerting a co-ordination number of six to form a group of 26 uter electrons, which is the same as the number found in the wo highest quantum groups of the next following inert gas 3 sub-groups of 6 and 2 of 4 electrons). Reference to Table XII n page 208 will make this point clear. On the other hand, the uadricovalent atoms build up 24 electrons in all cases shown n the table. Werner has shown that it is necessary to arrange he four groups in one plane, in order to account for the geo-netric isomers observed. This suggests that the octahedral ymmetry of the compounds where the co-ordination number is is maintained, two groups at the end of one diagonal being bsent.

Sidgwick also introduces the conception that electrons shared etween two atoms encircle both nuclei. Thus Nicholson only ound it possible to derive the spectrum of molecular hydrogen n the assumption that each electron executed an orbit of this ind. This point will be further considered in the following ection.

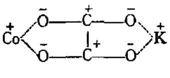
The limitations imposed on the maximum co-ordination umber of an atom form the basis of a rule due to Sidgwick.[50]

This is based upon the numbers of electrons in Bohr's quantum sub-groups, and may be formulated as follows: "The highest covalency number of an atom is that of the maximum size of the *sub-group* next to the largest completed group in the atom." Thus, if the atom has enough unshared electrons to fill n quantum groups completely, its maximum covalency is equal to the number of electrons in a sub-group of the $(n + 1)$th quantum group. For example, in hydrogen, there are insufficient electrons to fill the first quantum orbit, so that its maximum covalency should be, according to the rule, the same as that of the number of electrons of helium, which is 2, there being no sub-groups in this case. As observed, Lowry believes that hydrogen has this co-ordination number in many cases. From lithium to fluorine, $n = 1$, since there are insufficient electrons to fill the 2-quantum orbit, the maximum covalency should be 4, according to the rule, since this is the maximum number of electrons in a sub-group of the 2-quantum orbits. This is also supported by experiment. Similarly, from sodium to nickel (atomic number 28) $n = 2$, and thus the maximum covalency is 6, the maximum number of electrons in a Bohr sub-group of total quantum number 3. Thus no element before nickel can exert a higher covalency than 6, which again appears to be borne out by experiment. Between atomic numbers 28 and 60, a covalency not greater than 8 may be developed, and so on. This rule, it may be noted, will apply whether the electrons are distributed equally among the subdivisions of a quantum group, as in Bohr's scheme, or whether some other arrangement is postulated, so long as the maximum number of electrons in a sub-group is equal to twice the total quantum number of the group.

In this connection, it may be noticed that another scheme of distributing the electrons among the sub-groups has been advanced by Main Smith[53] and by Stoner.[54] It was observed (section 49, p. 205) that some difficulty is experienced in fitting in the absorption evidence with Bohr's quantum grouping, and further subdivision of the groups also appears to be necessary to account for the optical and X-ray emission spectra.[55] The results obtained by Dauvillier regarding the magnitudes of X-ray absorption discontinuities may provide evidence of another electron distribution. The sizes of the L absorption jumps were found to be approximately in the proportion 1 : 1 : 2. Assuming these magnitudes to be proportional to the number of electrons which absorb energy, the arrangement 2, 2, 4 fo

the L group is reached instead of the 4, 4 of Bohr. In this way, provision is made for three energy levels within the L level, as the absorption evidence requires. The completed M group may be written 2, 2, 4, 4, 6, and the N group 2, 2, 4, 4, 6, 6, 8 giving five and seven energy levels respectively. Thus the total number of electrons in a group is the same as in Bohr's arrangement, but the division into sub-groups is different. On this basis, Main Smith attempts to account for the relative stabilities of co-ordination compounds, by showing that the more stable compounds correspond with more symmetrical arrangements of sub-groups according to the scheme.

Lowry distinguishes between two types of co-ordination, which he calls "centric" and "cyclic" respectively.[56] The centric type is exemplified by the complex ammines, and the cyclic type by the acetylacetone compounds with metals. A group which can contribute two associating units to the co-ordination number of an atom by simultaneous application at two points round the atomic sphere has been termed a "chelate" (crab-like) group by Morgan. Co-ordination involving ring systems may be called chelate co-ordination.[57] An example is supplied by the compound which may be represented by the structure—



where the number of atoms in each ring is odd, so that alternate polarities are replaced by "crossed" polarities.

This discussion is closed with a passing reference to the double cyanides of potassium with iron and cobalt. The effective atomic numbers in these cases are given after their respective formulæ below :—

$K_4Fe(CN)_6$	36	$K_4Co(CN)_6$	37
$K_3Fe(CN)_6$	35	$K_3Co(CN)_6$	36

Here 36 is the atomic number of krypton, so that it is of interest to observe that this number of electrons confers stability, for potassium ferrocyanide is rather more stable in air than potassium ferricyanide, while potassium cobaltocyanide is readily oxidized, although the trivalent cobalt ion with 24 electrons is normally unstable.

56. Magnetic Theories: Concluding Considerations

The theories of atomic and molecular structure presented in the foregoing pages have almost entirely neglected the phenomena of magnetism. It is clear, however, that such theories are to this extent incomplete. An attempt must therefore be made to review some leading features of the present position in regard to magnetism.

It has long been known that a piece of iron placed between the poles of a magnet has magnetism induced in it. This occurs in such a way that the north induced pole of the iron is opposite to the south pole of the magnet, and the south induced pole of the iron opposite to the north pole of the magnet. The result may be expressed by saying that the iron has a positive susceptibility, this being measured by the ratio of the intensity of magnetization induced to the field strength. Faraday, however, discovered another class of substances, which behaved in the opposite way, so that north induced pole was opposite to north pole and south induced pole opposite to south pole. Such "diamagnetic" substances show a negative susceptibility.

It is customary, with Curie, to divide substances into three classes, according to their behaviour in a magnetic field, as follows:—[58]

Class.	Susceptibility.	Effect of Temperature.
I. Diamagnetic.	Negative; small.	Practically independent.
II. Paramagnetic.	Positive.	Varies inversely as the absolute temperature.
III. Ferro-magnetic.	Positive; larger than in II.	Varies in complex manner.

Langevin (1905) and Weiss (1907) presented theories to account for the varying behaviour of substances under magnetic influence. The former was concerned with substances of Classes I and II, and the latter more particularly with those of Class III.

According to Langevin, a molecule consists of a number of revolving positive and negative charges.[59] If the total moment is zero, the molecule is diamagnetic, but, if not, it is paramagnetic or ferro-magnetic. As long as no interaction occurs between different molecules, an explanation is offered of the effect of temperature upon the magnetization of diamagnetic and paramagnetic substances. Weiss considers the mutual action between molecules, which is marked in ferro-magnetic

substances.[60] He postulates an intrinsic molecular field, which may not necessarily have a magnetic origin. This field corresponds to the forces which determine crystallization, and may be regarded as a magnetic field, proportional to the intensity of magnetization, of strength of the order of 10^7 gauss. For many substances, Curie's rule of the effect of temperature in the case of paramagnetic substances holds approximately, the constant of proportionality frequently having, however, a series of values over different temperature ranges. Weiss considers that sudden changes of magnetic moment occur, which may be referred to a unit "magneton," whose moment is $18{\cdot}54 \times 10^{-22}$ C.G.S.E.M. unit.[61] It is possible, in certain cases, to assign "magneton numbers" to atoms; for example, the number in the case of iron is 11. No correspondence appears to exist between these numbers and the atomic numbers of Moseley, although recent evidence tends to show that the electron itself behaves as a magneton in atomic structure. This particular problem is at present far from being solved.

On the other hand, Bohr has developed the magneton conception on the basis of the dynamic theory of atomic structure. The unit magneton postulated has the moment of a 1_1 orbit of hydrogen. This unit is approximately five times that of Weiss, being given by—

$$M = \frac{e}{2mc} \cdot \frac{h}{2\pi} \qquad \qquad (6)$$

The Bohr magneton may be calculated as 5593 C.G.S.E.M. units per gram-atom, which value is a little less than five times the Weiss magneton (1124 in the same units). The magnetic moment of an orbit n_k is k times the Bohr unit.

Further, in addition to the characteristic total and azimuthal quantum numbers by means of which orbits may be defined, an "inner" quantum number has been introduced, as measuring the angular momentum of the atom as a whole, which depends on the relative orientation of the outer electron orbit and the central core. In a magnetic field the atoms tend to orientate in definite directions, and taking this into account, Pauli has calculated the Weiss numbers to be expected corresponding to different Bohr magneton numbers. The susceptibilities of nitric oxide and of oxygen may be in this way explained by assigning to these gases 1 and 2 Bohr magnetons respectively.[62] This conception has been developed by Sommerfeld, who has shown that Pauli's "space quantization" leads to simple

relationships between the numbers of Bohr magnetons in the ions in solution of the elements from potassium to copper in the periodic system, as in Table XXII.[63]

TABLE XXII

Bohr Magneton Numbers (Sommerfeld)

Ion.	No. of Electrons.	No. of Bohr Magnetons.
K^{+}, Ca^{++}	18	0
Ti^{+++}	19	1
Cr^{+++}	21	3
Cr^{++}, Mn^{+++}	22	4
Mn^{++}, Fe^{+++}	23	5
Co^{++}	25	4
Ni^{++}	26	2
Cu^{++}	27	1
Cu^{+}	28	0

Thus, according to the table, the number of magnetons reaches a maximum for the ions Mn^{++} and Fe^{+++} with 23 electrons, decreasing regularly on each side, by steps of one unit. Now the use of the inner quantum number has enabled schemes of energy levels to be drawn up, which appear to accord with *experimental data relating to optical and X-ray spectra*, and with which the above results may be closely correlated.[64] It is just in the iron region that, according to the proposed scheme, the balance of the magnetic effects of the orbits is first disturbed by the addition *of electrons to the* M_{IV} and M_V sub-levels, and then restored as the groups are completed. It has been already noticed that this scheme of distribution of electrons in the sub-groups is in accord with that suggested by Main Smith (p. 254). The significance of spectroscopic magneton numbers has been discussed by Stoner.[64]

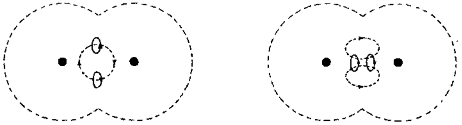
On the other hand, a certain amount of experimental evidence has been considered to favour a static rather than a dynamic interpretation of atomic and molecular structure. Thus Oxley has developed the conception of electrons moving in small orbits to explain paramagnetic and diamagnetic linkages, as depicted in Fig. 43.[65] A model of this kind is made the basis of an explanation of the deportment of crystals in a magnetic

field. Oxley considers that the success of the Bohr-Sommerfeld theory is limited to the simplest types of atoms, namely, hydrogen and singly-ionized helium, and that such atoms are during the emission of radiation in an abnormal state compared with that which exists in unexcited matter, upon which the magnetic determinations have been conducted. The cubical atom model of Langmuir and Lewis is thought to give a clearer picture of the nature of diamagnetism and paramagnetism than the Bohr theory with " its large unbalanced electron orbits." Oxley adds: " Some factor seems to have been neglected in Bohr's theory, which, though of small importance when the atoms contain each only one electron and are independent of each

Figure XLIII

PARAMAGNETIC AND DIAMAGNETIC COUPLING (OXLEY)

(*Proc. Roy Soc.*, 1921; A 98, 265)



The black dots indicate diffuse atomic kernels, consisting of positive charges and a spatial distribution of electrons, supposed to be rotating in small circles at varying distances from the atomic nuclei. The first diagram indicates a paramagnetic, and the second a diamagnetic linkage.

other, yet is of primary importance for matter in its normal state, and without which it is impossible to explain either the magnetic properties of crystals or crystal structure."

This discussion is concluded by noticing a few other results which bear, directly or indirectly, upon the subject of magnetic phenomena. Oxley has found that when palladium absorbs hydrogen, a system is formed having an electronic configuration like that of the element one higher in atomic number, namely silver, by the entrance of the negative electron of a hydrogen atom into the outer system of the palladium atom. Thus palladium is paramagnetic, while palladium containing hydrogen is diamagnetic like silver. Similarly, while pure manganese is paramagnetic, manganese fused in hydrogen is ferro-magnetic,

iron being one unit higher in atomic number than manganese.[66] This evidence is interpreted on the basis of the Lewis-Langmuir atomic model.

In 1922, Whittaker published a new quantum mechanism based on the postulate of a number of magnetic doublets within the atom.[67] If an electron collides with this system, the collision is elastic if the velocity of the electron is less than a critical value. If this limit is exceeded, however, the electron gives up a definite amount of energy, which is identified with Planck's quantum. By means of this, an expression for the Balmer series of hydrogen lines is deduced.

Pascal observed (1910) that the molecular magnetic susceptibilities of organic compounds were the same as the sum of the individual atomic susceptibilities, while with ionized compounds this was not the case. This suggests some difference between the two kinds of linkage from the magnetic point of view. The ionized linkage is electrostatic in character, and offers no special difficulties. The non-ionized linkage, where, according to Lewis, electrons are shared, is not quite so clearly and certainly understood. Oxley postulates the arrangement shown in Fig. 43. On the other hand, with Fajans and Knorr and others, it may be supposed that the linking electrons execute orbits which encircle both nuclei.[68] The chemical evidence seems to require a continuous gradation between the two kinds of linkage.[69] This is readily interpreted on the basis of the Lewis theory by the shifting of the electron pair. In the non-polar linkage, the pair may be symmetrically placed with regard to the two nuclei, while in the polar linkage the pair of electrons is displaced in the direction of the anion, providing the required continuity. It might appear to be rather more difficult to maintain this with a dynamic model. Yet it is a very definite part of the theories of Fajans and of Knorr that this is possible. Thus, Fajans supposes that the electron shell of an anion may be deformed to some extent by the influence of the cation, and the deformation may be so great that the electron may be attracted so as to describe an orbit round both nuclei and provide a polar link. This conception has been developed by Knorr. A dynamic model has recently been published by Morgan, which seems to supply a picture of the way in which this may happen.[70] Morgan considers the movement of electrons upon equipotential surfaces, which he regards as a necessary consequence of Bohr's theory of the repression of energy emission in an orbit. For the hydrogen molecule, these surfaces are represented in section in

Fig. 44. The group of curves is that associated with the name of Cassini, and is given, in "bi-polar co-ordinates," by the equation—

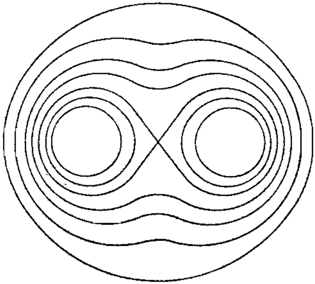
$$V = \frac{e}{r} + \frac{e}{r_1} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V is the potential (a constant for each curve of the series), e is the charge on each hydrogen nucleus, and r, r_1 are the distances from the two nuclei of any point on the curve. This system of curves is divided into an inner and an outer group,

FIGURE XLIV

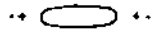
CASSINIAN OVALS

(*Chem. and Ind.*, 1924; **43**, 1071)



the critical condition being the figure-of-eight curve, the lemniscate of Bernouilli. There are outer Cassinian ovals corresponding with non-polar linkages, and inner ovals corresponding with polar linkages. Although there may be a distinct difference between the extreme types, there is also the continuous gradation required by the chemical evidence. It may be doubted, however, whether such a model will be acceptable to the mathematical physicist, but it provides, provisionally at any rate, a description of the kinds of linkage with which the chemist is familiar.

Knorr distinguishes between four types of binding between atoms, as follows, where the curved lines represent electron orbits :—

Type of Link.	Example.	Diagrammatic Representation.
1. Covalent.	Diamond.	
2. Electrovalent.	Lithium fluoride.	
3. Molecular.	Ice.	
4. Metallic.	Sodium.	

In connection with the conception of " rings " of electrons in heavier atoms, it is worthy of note that other arrangements than the generally accepted 2 electrons for the K ring and 8 electrons for the L ring have, from time to time, been suggested. Thus W. L. Bragg, James and Bosanquet found that the intensity of X-radiation reflected by sodium chloride could be interpreted on the basis of the sodium ion possessing rings of 3 and 7 electrons and the chlorine ion rings of 3, 5 and 10 electrons from the nucleus outwards.[71] Similarly, on X-ray spectroscopic grounds, Debye has concluded that the K ring contains 3 electrons in its normal state.[72] It appears possible that these results are statistical mean values, when, with Bohr, the possibility of penetration of the orbits of electrons bound earlier than the penetrating electron is admitted. The chemical evidence is consistent with Kossel's view, which provides rings of 2 and 8 for the sodium ion, corresponding with the stable structures of helium and neon. It becomes clear that, much as it may seem desirable, it is impossible to contemplate separate independent rings of electrons. The atom is an entangled system, by no means as simple as some models might lead us to suppose. Bearing this in mind, however, such models may still be useful, and lead in many cases to clear visualization.

The conception of rings of electrons of the Bohr type appears insufficient to explain the results of Born and Landé on the compressibility of crystals of the alkali halides (p. 69). These authors have shown that the observed compressibilities may be accounted for if the ions of these crystals attract each other in the cubic lattice according to the inverse square law, and repel each other with a force varying inversely as the *ninth* power of the distance between their centres.[73] Bohr's theory is found to give rise to a different law when applied to crystals, the repulsive force varying inversely as the *fifth* power of the distance, and yields compressibilities about twice as great as those observed.[74] Born, therefore, discards Bohr's model, and shows that the

cubic model with restricted or localized electron orbits leads to the correct law of force, and thus accounts for the compressibilities.[75] This work suggests that orbits of a totally different kind from those postulated by Bohr may have to be considered by mathematical physicists in connection with atoms which have more than one electron. As already pointed out, Bohr's theory has supplied a complete account of spectroscopic facts only for atoms having one electron. With the neutral helium atom, difficulties appear which are not yet solved. Langmuir has calculated the ionization potential of helium by assuming a model in which the electrons, on account of mutual repulsion, retrace their paths, oscillating in arcs of approximately circular form.[76] It appears, then, that the dynamics of "spatial orbits" of localized type, different from those defined by the inner quantum number, for instance (where the orientation of the orbit is taken into account, but where the orbits are of Bohr type and the orbital planes always contain the nucleus) will have to be more closely considered in the future. This field is at present almost entirely unexplored.

With regard to the limitations of Bohr's theory, it should be remembered that the theory applies primarily to isolated atoms. It is interesting that physical evidence should point to a model of the Lewis type for atoms in combination, as in crystals, for this model has been specially successful in explaining chemical relationships, as shown in this chapter. The models of Lewis and Langmuir, though usually called "static," allow for restricted movement such as oscillation about a central position.

Laurie has given some suggestions for a valency theory in terms of magnetons.[77]

The theories outlined in this chapter may present a somewhat perplexing array to the reader. This must be partly attributed to the immaturity of the electronic theory of valence. Still, it must be recognized that a beginning has been made. The researches of Rankine and Smith and others have provided an experimental basis for the octet theory of atomic structure, which has figured so largely in the argument. The extensions of this theory to mixed bonds, crossed bonds and alternating polarities seem to possess value, and some experimental support has been cited. These theories, however, encounter many difficulties, and at present there exists no universal agreement concerning them. It may, therefore, be advisable to restate those conclusions which appear to be generally accepted. The five groups of statements given below rest upon experimental

evidence and provide a nucleus round which theories may be built.

(1) There are two kinds of chemical union, polar and non-polar. *Non-polar union is due to the sharing of electrons.* (It seems to be certain that the sharing of electrons postulated in static theories will be interpreted in the dynamic models by the sharing of electron orbits.)[78] The gradation between the two kinds of union is continuous.

(2) The extranuclear arrangements of the inert gases are particularly stable, other groupings tending to revert to them when possible.

(3) Atoms in general exhibit two kinds of valency, principal valency and contravalency, such that the sums of their maximum possible values are equal to eight.

(4) The larger the charge on an ion and the smaller its volume, the greater is its tendency to form stable groupings in combination.

(5) Certain compounds, such as ethylene, may exist in at least two states, a reactive state and an inactive state. The suggestion that the reactive state in the case of ethylene is due to polarization of the molecule is supported by experiment.

Considerable controversy exists between those who support static and those who favour dynamic views of atomic structure. It is not now suggested in the dynamic theories, however, that the orbits of different electrons in the same atom lie in one plane, and this seems to supply the measure of electronic independence required in the static theories; although, as already mentioned, other "spatial" orbits may exist. It appears probable that the present difference of opinion will end, as in other well-known cases, with honours on both sides, and as the nineteenth century was marked by the evolution of the atomic theory, so the twentieth will be associated with the rise and development of the theory of atomic structure.

REFERENCES: (IX)

[illegible]. 10, 14, 17, *and* 19 *in Bibliographical List at end of book*

1 (p. 212) J. J. Thomson: "The Forces between Atoms and Chemical Affinity"; *Phil. Mag.*, 1914; (vi.) **27**, 757.

2 (p. [illegible]) G. N. Lewis: "Valence and Tautomerism"; *J. Amer. Chem. Soc.*, 1913; **35**, 1448.

3 (p. 214) *Idem*: "The Atom and the Molecule"; *J. Amer. Chem. Soc.* 1916; **38**, 762.

4 (p. 214) W. Kossel: "Über Molekülbildung als Frage des Atombaus"; *Ann. Physik*, 1916; (iv.) **49**, 229.
Idem: "Bemerkungen über Atomkräfte"; *Z. Physik*, 1920; **1**, 395.
5 (p. 214) R. Abegg and G. Bodländer: "Die Elektroaffinität, ein neues Prinzip der chemischen Systematik"; *Z. Anorg. Chem.*, 1899; **20**, 453
R. Abegg: "Die Valenz und das periodische System. Versuch. einer Theorie du Molekularverbingungen"; *Z Anorg. Chem.*, 1904; **39**, 330.
6 (p. 220) J. J. Thomson: "On the Structure of the Atom"; *Phil., Mag.*, 1904; (vi.) **7**, 237.
7 (p. 221) *Idem*: Romanes Lecture, 1914.
8 (p. 221) *Idem*: "On the Structure of the Molecule, and Chemical Combination"; *Phil. Mag.*, 1921; (vi.) **41**, 510.
9 (p. 222) *Idem*: "On the Structure of the Atom"; *Phil. Mag.*, 1913; (vi.) **26**, 792.
Idem: "On the Origin of Spectra and Planck's Law"; *Phil. Mag.*, 1919; (vi.) **37**, 419.
10 (p. 222) J. R. Rydberg: "The Ordinals of the Elements and the High Frequency Spectra"; *Phil. Mag.*, 1914; (vi.) **28**, 144.
11 (p. 223) I. Langmuir: "The Arrangement of Electrons in Atoms and Molecules"; *J. Amer. Chem. Soc.*, 1919; **41**, 868.
Idem: "The Stucture of Atoms and the Octet Theory of Valence"; *Proc. Nat. Acad. Sci.*, 1919; **5**, 252.
12 (p. 223) Discussion on the Structure of Molecules: *Brit. Ass. Rep.*, 1921; 468.
13 (p. 224) T. M. Lowry: "The Uniqueness of Hydrogen"; *Chem. and Ind.*, 1923; **42**, 43.
14 (p. 227) A. O. Rankine: "On the Proximity of Atoms in Gaseous Molecules"; *Proc. Roy. Soc.*, 1921; **A98**, 360.
15 (p. 227) *Idem*: "On the Similarity between Carbon Dioxide and Nitrous Oxide"; *Proc. Roy. Soc.*, 1921; **A98**, 369.
C. J. Smith: "Viscous Properties of CO_2, N_2O, CO and N_2"; *Proc. Phys. Soc.*, 1921; **34**, 155.
16 (p. 229) I. Langmuir: "Isomorphism, Isosterism and Covalence"; *J. Amer. Chem. Soc.*, 1919; **41**, 1543.
17 (p. 229) A. W. Hull: "A New Method of Chemical Analysis"; *J. Amer. Chem. Soc.*, 1919; **41**, 1168.
18 (p. 229) C. J. Smith: "On the Viscosity and Molecular Dimensions of Hydrogen Selenide"; *Trans. Farad. Soc.*; 1923, **18**, 302.
19 (p. 231) J. C. McLennan: "The Spectrum of Ionized Potassium"; *Proc. Roy. Soc.*, 1921; **A100**, 182.
Idem: "The Spectra of the Lighter Elements"; *Nature*, 1924; **113**, 217.
A. Fowler: "The Series Spectrum of Trebly Ionized Silicon (Si IV)"; *Proc. Roy. Soc.*, 1923; **A103**, 413.
F. Paschen: "Die Funkenspektren des Aluminium"; *Ann. Physik*, 1923; (iv.) **71**, 142.
I. S. Bowen and R. A. Millikan: "The Series Spectra of the Stripped Boron Atom"; *Proc. Nat. Acad. Sci.*, 1924; **10**, 199. See also: *Phys. Rev.*, 1924; **23**, 1.
D. R. Hartree: "The Spectra of some Lithium-like and Sodium-like Atoms"; *Proc. Camb. Phil. Soc.*, 1924; **22**, 409, 464.

20 (p. 231) W. L. BRAGG: "Atomic Arrangement in Crystals"; *Phil. Mag.*, 1920; (vi.) **40**, 169.

21 (p. 232) R. W. G. WYCKOFF: "On the Hypothesis of Constant Atomic Radii"; *Proc. Nat. Acad. Sci.*, 1923; **9**, 33.

22 (p. 232) I. LANGMUIR: "*Forces within a Static Atom*"; *Phys. Rev.*, 1921; (ii.) **18**, 104.

23 (p. 232) C. R. BURY: "Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules"; *J. Amer. Chem. Soc.*, 1921; **43**, 1602.

24 (p. 232) T. M. LOWRY: "The Electronic Theory of Valency. Part I. Intramolecular Ionization"; *Trans. Farad. Soc*, 1923; **18**, 285.

25 (p. 234) E. B. R. PRIDEAUX: "The Structure of the Halides and Oxides of the 5th, 6th, and 7th Groups"; *Chem. and Ind.*, 1923; **42**, 672.

26 (p. 234) J. J. THOMSON: See Ref. No. 8.

27 (p. 237) T. M. LOWRY: "A Plausible Error in the Theory of Co-ordination"; *Chem. and Ind.*, 1923; **42**, 623.

28 (p. 237) E. D. EASTMAN: "Double and Triple Bonds, and Electron Structures in Unsaturated Molecules"; *J. Amer. Chem. Soc.*, 1922; **44**, 438.

29 (p 237) R. ROBINSON: Discussion on Intramolecular Ionization; *Trans. Farad. Soc.*, 1923; **18**, 299.

30 (p. 237) T. D. STEWART and K. R. EDLUND: "The Rate of Reaction between Ethylene and Bromine"; *J. Amer. Chem. Soc.*, 1923; **45**, 1014.

31 (p. 237) R. G. W. NORRISH: "Studies of Electrovalency. III. The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine"; *J. Chem. Soc., Trans.*, 1923; **124**, 3006.
Idem: "The Mechanism of Chemical Activation"; *Chem. and Ind.*, 1924; **43**, 327.

32 (p. 237) A. STOCK, E. KUSS and O. PRIESS: "Borwasserstoffe. V. Die Einwirkung von Chlor und Brom auf B_2H_6 und $B_{10}H_{14}$. Die Wertigkeit des Bors"; *Chem. Ber.*, 1914; **47**, 3115.

33 (p. 237) T. M. LOWRY: "Studies of Electrovalency. Part I. The Polarity of Double Bonds"; *J Chem. Soc., Trans.*, 1923; **123**, 822.

34 (p 238) S. SUGDEN: "Electron Valency Theories and Stereochemistry"; *J. Chem. Soc., Trans.*, 1923; **124**, 1861.

35 (p. 238) T. M. LOWRY: "Note on the Theory of Free Rotation"; *J. Chem. Soc., Trans.*, 1923; **124**, 1866.

36 (p. 239) *Idem*: "Co-ordination and Acidity"; *Chem. and Ind.*, 1923; **42**, 1048.

37 (p. 241) R. M. CAVEN: "The Basic Strength of Ammonia and Allied Bases"; *Chem. and Ind.*, 1923; **42**, 164.

38 (p. 242) T. M. LOWRY: "The Electronic Theory of Valency. III"; *Phil. Mag.*, 1923; (vi.) **46**, 1013.

39 (p. 242) B. FLÜRSCHEIM: "Ueber die Addition von Alkohol an Nitroderivate des Styrols"; *J. für Prakt. Chem.*, 1902; **66**, 16.
Idem: "The Electronic Theory of Valency"; *Phil. Mag.*, 1924; (vi.) **47**, 569.

40 (p. 243) A. LAPWORTH: "A Theoretical Derivation of the Principle of Induced Alternate Polarities"; *J Chem. Soc., Trans.*, 1922; **121**, 416. See also: *Idem*: *Mem. Manch. Phil. Soc.*, 1920; (ii.) **64**, 1.

41 (p. 243) W. O. KERMACK and R. ROBINSON: "An Explanation of the Property of Induced Polarity of Atoms, and an Interpretation of the Theory of Partial Valencies on an Electronic Basis"; *J. Chem. Soc., Trans.*, 1922; **121**, 427.

42 (p. 244) A. LAPWORTH and J. B. SHOESMITH: "Reciprocal Induced Polarity Effects in Cresols and their Derivatives. Properties of the Isomeric Methoxybenzylbromides"; *J. Chem. Soc., Trans.*, 1922; **121**, 1391.

43 (p. 245) H. HENSTOCK: "Nuclear Tubes of Force and Bonds of Variable Polarity in an Atom"; *Trans. Farad. Soc.*, 1923; **19**, 508.

44 (p. 246) T. M. LOWRY and H. BURGESS: "Studies of Electrovalency. Part II. Co-ordinated Hydrogen"; *J. Chem. Soc., Trans.*, 1923; **124**, 2111.

45 (p. 246) W. M. LATIMER and W. H. RODEBUSH: "Polarity and Ionization from the Standpoint of the Lewis Theory of Valence"; *J. Amer. Chem. Soc.*, 1920; **42**, 1431.

46 (p. 247) A. HANTZSCH: "Über die Konstitution der Carbonsäuren sowie über die optischen und chemischen Vorgänge bei der Bildung von Estern, Salzen und Ionen"; *Chem. Ber.*, 1917; **50**, 1422.

47 (p. 247) G. T. MORGAN and J. D. MAIN SMITH: "Researches in Residual Affinity and Co-ordination. Part X. Salicylatotetramminocobaltic Salts and the Constitution of Oxonium Compounds"; *J. Chem. Soc., Trans.*, 1922; **121**, 1956.

48 (p. 249) N. V. SIDGWICK: "The Bohr Atom and the Periodic Law"; *Chem. and Ind.*, 1923; **42**, 901.

49 (p. 250) *Idem*: "Co-ordination Compounds and the Bohr Atom"; *J. Chem. Soc., Trans.*, 1923; **123**, 725.

50 (p. 252) C. H. SPIERS: "The Electron Theory of Valency applied to Co-ordination Compounds"; *Chem. and Ind.*, 1923; **42**, 534.

51 (p. 252) C. J. BROCKMAN: "The Theory of Co-ordination and the Lewis-Langmuir Structure of the Atom"; *Chem. and Ind.*, 1924; **43**, 756.

52 (p. 253) N. V. SIDGWICK: "The Bohr Atom and Covalency"; *Chem. and Ind.*, 1923; **42**, 1203.

53 (p. 254) J. D. MAIN SMITH: "Atomic Structure"; *Chem. and Ind.*, 1924; **43**, 323.

54 (p. 254) E. C. STONER: "The Distribution of Electrons among Atomic Levels"; *Phil. Mag.*, 1924; (vi.) **48**, 719.

55 (p. 254) N. BOHR and D. COSTER: "Röntgenspektren und periodischen System der Elemente"; *Z. Physik*, 1923; **12**, 342.

56 (p. 255) T. M. LOWRY: "Stability of Co-ordination Compounds"; *Chem. and Ind.*, 1923; **42**, 711.

57 (p. 255) J. D. MAIN SMITH: "Chelate Co-ordination"; *Chem. and Ind.*, 1923; **42**, 847.

58 (p. 256) P. CURIE: "Propriétés magnétiques des corps à diverses températures"; *J. Physique*, 1895; (iii.) **4**, 197, 263.

59 (p. 256) P. LANGEVIN: "Sur la théorie du magnétisme"; *J. Physique*, 1905; (iv.) **4**, 678.

60 (p. 257) P. WEISS: "La variation du ferromagnétisme avec la température"; *Compt. Rend.*, 1906; **143**, 1136.

61 (p. 257) *Idem*: "Sur la rationalité des rapports des moments magnétiques des atomes, et un nouveau constituant universel de la matière"; *Compt. Rend.*, 1911; **152**, 187, 367.

62 (p. 257) W. PAULI: "Quantentheorie und Magneton"; *Phys. Z.*, 1920; **21**, 615.

63 (p. 258) A. SOMMERFELD: "Zur Theorie des Magnetons"; *Z. Physik*, 1923; **19**, 221. See also: W. GERLACH: "Bohrsches und Weissches Magneton"; *Phys. Z.*, 1923; **24**, 275; and A. SOMMERFELD: "Spektroskopische Magnetonezahlen"; *Phys. Z.*, 1923; **24**, 360.

64 (p. 258) E. C. STONER: "The Significance of Spectroscopic Magneton Numbers"; *Phil. Mag.*, 1925; (vi.) **49**, 1289.

A. LANDÉ: "Termstruktur und Zeemaneffekt der Multipletts"; *Z. Physik*, 1923; **15**, 189: **19**, 112.

A. SOMMERFELD: "Zur Theorie der Multipletts und ihrer Zeemaneffekte"; *Ann. Physik*, 1924; (iv.) **73**, 209.

65 (p. 258) A. E. OXLEY: "Magnetism and Atomic Structure"; *Proc. Roy. Soc.*, 1921; **A98**, 264.

66 (p. 260) *Idem*: "Magnetism and Atomic Structure. II. The Constitution of the Hydrogen-Palladium System and other similar Systems"; *Proc. Roy. Soc.*, 1922; **A101**, 264.

67 (p. 260) E. T. WHITTAKER: "The Quantum Mechanism in the Atom"; *Proc. Roy. Soc. Edin.*, 1922; (ii.) **42**, 129.

68 (p. 260) K. FAJANS: "Struktur und Deformation der Elektronenhüllen in ihrer Bedeutung für die chemischen und optischen Eigenschaften anorganischer Verbindungen"; *Naturwiss.*, 1923; **11**, 165.

C. A. KNORR: "Eigenschaften chemischer Verbindungen und die Anordnung der Elektronenbahnen in ihren Molekülen"; *Z. Anorg. Chem.*, 1923; **129**, 109.

69 (p. 260) S. H. C. BRIGGS: "The Valency Bond. Electrovalence and Covalence"; *Phil. Mag.*, 1924; (vi.) **47**, 702.

70 (p. 260) G. T. MORGAN: "A Dynamic Hypothesis of Chemical Combination"; *Chem. and Ind.*, 1924; **43**, 1071.

71 (p. 262) W. L. BRAGG, R. W. JAMES, and C. H. BOSANQUET: "The Distribution of Electrons around the Nucleus in the Sodium and Chlorine Atoms"; *Phil. Mag.*, 1922; (vi.) **44**, 432. See also: "The Intensity of Reflexion of X-Rays by Rock-Salt"; *Phil. Mag.*, 1921; (vi.) **41**, 309: (vi.) **42**, 1.

72 (p. 262) P. DEBYE: "Die erste Elektronenring der Atome"; *Phys. Z.*, 1917; **18**, 276. See also: J. KROO: *Phys. Z.*, 1918; **19**, 307.

73 (p. 262) M. BORN and A. LANDÉ: "Über die Berechnung der Kompressibilität regulärer Kristalle aus der Gittertheorie"; *Verh. Deut. Phys. Ges.*, 1918; **20**, 210.

74 (p. 262) *Idem*: "Kristallgitter und Bohrsches Atommodell"; *Verh. Deut. Phys. Ges.*, 1918; **20**, 202.

75 (p. 263) M. BORN: "Über kubische Atommodelle"; *Verh. Deut. Phys. Ges.*, 1918; **20**, 230.

A. LANDÉ: "Würfelatome, periodisches System und Molekülbildung"; *Z. Physik*, 1920; **2**, 380.

76 (p. 263) I. LANGMUIR: "The Structure of the Helium Atom"; *Science*, 1920; **51**, 605.

77 (p. 263) A. P. LAURIE: "Suggestions for a Magnetic Theory of Valency"; *Trans. Farad. Soc.*, 1924; **20**, 1.

78 (p. 264) N. R. CAMPBELL: "A Static or Dynamic Atom?"; *Nature*, 1923; **111**, 569.

CHAPTER X

THE PRESENT OUTLOOK

57. The Theory of Relativity

THE development of scientific thought described in the foregoing pages, respecting the constitution of matter and the nature of energy, is leading to a new and different outlook upon familiar physical conceptions. Mental habits are changing and evolving upon lines which could hardly have been foreseen.

The theory of relativity of Einstein, in particular, suggests that many hereditary habits of thought must be discarded, as the nature and operation of natural laws are progressively understood. The conclusions of this theory have been used from time to time, and a short discussion of it may be useful here. Only a few suggestions, however, will be offered, which can be followed up if desired.

It has long been known that the apparent velocity of a body depends on the state of motion of the observer. Newton's dynamical laws, however, embodied in the relations between forces, masses, and accelerations, hold equally well for a system at rest or for one moving with uniform velocity. There is, therefore, no means of determining from ordinary dynamical experiments whether a system is at rest or in uniform motion in absolute space.

The question, therefore, naturally arises whether there exists any means of determining the absolute velocity of a body, such as the earth, through space. It was formerly thought that experiments on the velocity of light might provide the required information. According to ordinary electrodynamical theory, the velocity of light in space is a constant c, so that the velocity measured by an observer moving in the direction of propagation should be less, and by one moving in the opposite direction greater, than c. The classical experiment of Michelson, however, performed in 1881, and repeated by him and Morley in

1887, showed that the measured velocity of light is independent of the motion of the observer.[1] A number of different types of experiments have been tried to detect absolute motion, but all have given a negative result.

The relativity theory does not attempt to "explain" this; it makes the impossibility of determining absolute motion its basic postulate, of which the Michelson-Morley result is a particular example. The laws and equations expressing the relations between phenomena are independent, according to the postulate, of the state of motion of the observer.

In the *special* theory, only uniform relative motion of observers and systems is considered. To satisfy the above basic principle (which involves an identical measured velocity of light for different observers) both length and time measurements must be supposed to depend upon the motion of the observer. These vary so that in the Michelson-Morley experiment the ratio of the lengths and times involved in the determination of the velocity of light remains constant.

The changes which occur in the measurements of time and distance made by two observers, one of whom is moving relatively to the other, can be considered as follows. Space and time are relative. The position of a point in space is usually defined by three co-ordinates, x, y and z, referred to some point as origin, through which three axes of reference pass. Minkowski has added a fourth co-ordinate of time t, which may be referred to a "zero" time. An "event" is then completely defined in space and time by four co-ordinates, x, y, z and t. Precision is gained by speaking of "space-time" instead of "space and time." An event happening at a certain place at no time is as meaningless as an event happening at a certain time but at no position in space. Space and time are separated through habits of thought, but they are really inseparably blended in the "space-time continuum" of Minkowski. The idea of a co-ordinate system, or "frame of reference," in such a continuum is introduced. In reality, however, no frame of reference absolutely fixed in the continuum is known, and it is only possible to refer an event to a frame of reference defined in some way. The special theory of relativity suggests that when an observer moves he divides the space-time intervals differently into space and time, so that his measurements of time and distance are altered. The effect is usually too small to be detected, but it becomes appreciable with velocities approaching the speed of light, as with β-rays.

This theory also proposes to identify mass with energy (see

section 41). The energy of a body consists of a constant amount due to its " rest-mass " plus a variable amount, which is, for slower motions, represented by the kinetic energy as defined in ordinary mechanics. Thus, the mass of a body depends upon its kinetic energy, which depends in turn upon its velocity, so that mass depends upon motion and increases with increasing kinetic energy. The mass of a body is greater if it is moving than if it is at rest, as judged from a given frame of reference. Similarly, if it receives energy E without change of velocity, its mass increases by an amount E/c^2, where c is the velocity of light. The conception of relativity of mass has been used in connection with β-rays (section 22, p. 94), the change of mass in building up an atom of helium (section 41, p. 159), and the energy of electronic orbits with high eccentricity (section 48, p. 198).

The special theory deals with frames of reference moving relatively to each other with uniform velocity. In the *general* theory, however, Einstein deals with frames of reference moving relatively to each other with variable velocity. Thus the basic relativity postulate, the impossibility of detecting absolute motion, is extended to systems moving relatively to each other in any way whatever. For any observer there will be a space-time frame of reference to which events will be referred. Now, the Newtonian system of mechanics is based upon the laws of motion, the first of which postulates that uniform motion in a straight line needs no explanation. Deviations from this state of motion are referred to forces. Einstein suggests, however, that the nature of the particular space-time continuum frame of reference accounts for such deviations. Newtonian gravitational forces, for example, may be reinterpreted as arising from, or equivalent to, a " warping " of the space-time continuum. The presence of matter affects the neighbouring continuum, and, in a sense, matter is equivalent to warping of the space-time field. The nature of the warping, and hence the *characteristics of the gravitational field*, can be uniquely determined from certain complicated geometrical considerations, and the application of the relativity postulate. As a particular application of the theory, it may be shown that light rays will be bent in passing through the strong gravitational field near the sun. This has been confirmed by experiment during two eclipses, the amount of bending corresponding with the prediction by theory.

The general theory has also been successful in explaining the

motion of the perihelion of Mercury, the planet nearest to the sun. According to the Newtonian theory, the elliptic orbit of a planet due to the sun's attraction is fixed, and the rotation of the major axis of the orbit, which is found to exist, is explained by the disturbing effects produced by the other planets. It was found, however, that the latter effects only accounted for a portion of the observed rotation in the case of the planet Mercury. According to the Einstein theory, the sun's attraction would of itself produce a rotation of the major axis of the elliptic orbit in the same sense as its orbital motion, the motion amounting, in the case of Mercury, to 43 seconds of arc per century. This agrees very well with the previously unexplained residual motion of the perihelion of the planet's orbit. The theory also predicted a displacement towards the red of the spectral lines of atoms of an element at the surface of a star as compared with the corresponding lines observed at the surface of the earth. Experimental proof of this may now be said to have been supplied, though the matter was for a long time in doubt. Further discussion of this subject would unduly lengthen this description. It is hoped that the outline given will suggest thoughts about relativity on the right lines. It may be remarked that many of the paradoxes supposed to result from this theory are at fault, because the *mutual* relative motion of observer and observed is not taken into account. A list of some leading papers and books on relativity is appended.[9]

58. Limits of Applicability of Calculus and Thermodynamics

Attention is now called to certain facts, which are seldom sufficiently emphasized. There are at least two methods, of great power in other directions, which are of limited applicability to the problem of atomic structure. It may solve some difficulties, and prevent the possibility of certain mistakes, if these matters are discussed in this section.

It is proposed to consider first the limited applicability of the methods of the Differential Calculus, which is concerned with the "differentiation" of functions. It is well known that some functions are not differentiable. The possibility of the differentiation of a function depends roughly, let us say, upon its "continuity." If y is a function of x, then y can only be differentiated with respect to x if y is a continuous function of x, such that an infinitely small change in x produces a corresponding infinitely small change in y. Further, if y is a continuous func-

tion, it should be possible to divide it up into an *infinite* number of parts of the same kind; the reverse process of "integration" involves the recombination of these divided parts. Now, the classical idea of matter was that it was differentiable in this sense, that is, it could be split up into an infinite number of parts of the same nature. The modern theory of atomic structure leads, however, to the view that matter possesses what we may term an infinitely granular structure. The unoccupied space between atoms and within atoms is immensely greater than the volume occupied by electrons or atomic nuclei. Matter is, therefore, discontinuous in the mathematical sense of the word, and the machinery of the Differential and Integral Calculus has a limited applicability. This method can be used in considering the approach of an α-particle to a heavy nucleus, or the work done in moving an electron against the attractive force of a nucleus, as in section 46 (p. 181), for, in these cases, the force is assumed to be a continuous function of the distance. In general, however, it is clear that such methods are inapplicable to the problem, and another branch of mathematics, such as that of statistical mechanics, must be employed.

Another valuable method, which is limited in scope in connection with the problem in hand, is the doctrine of energy built up in the system known as "Thermodynamics." Attention was called, in section 3 (p. 7), to the fact that the perpetual movement of the molecules of matter is in conflict with thermodynamical principles. According to the Second Law, which is based on practical experience, no contrivance exists for converting heat of uniform temperature into work. A ship cannot be propelled by cooling the sea; it must, in practice, work between two temperatures. A locomotive works between the temperature of the boiler and that of the condenser, and can convert a certain proportion of the energy received at the higher temperature into work. Yet a molecule appears to be able to take energy for movement from its surroundings by cooling them, in contradiction with the principle. The molecule is capable of perpetual motion by virtue of this fact; it receives energy for movement from its surroundings, and delivers back the same amount at a later stage. The Second Law of Thermodynamics is, however, a "macroscopic" law, being derived from experience on our own dimensional scale. It may or may not apply to the atomic world, so far as experience goes; according to the evidence supplied by the Brownian movement, it certainly

does not apply there. If human beings were no bigger than bacteria, says Perrin, they might be able to catch hold of a molecule and stop it, and have a means of converting heat of uniform temperature into work. The result of these considerations, therefore, is that the principle of Carnot, while remaining true for magnitudes of which there is sensible knowledge, is *inapplicable to the small dimensions encountered in dealing* with atoms and molecules.

59. Theories of Matter, Energy, and the Æther[3]

The results set forth in this volume will reveal, when they are carefully considered, entirely new views of the nature and relationship of the two entities, matter and energy. The old "*dualistic*" hypothesis regarded them as quite distinct and sharply separated by the fact that the former alone possessed mass or inertia. At the time when the theory flourished, however, it was seen to involve difficulty, for it was not easy to imagine how energy, if it had no mass, could act upon matter at all.

The three following conclusions are supported by more recent work, and each is in direct conflict with the dualistic view.

(1) *Energy possesses inertia.*—A negative electron, which is the unit of electrical energy, possesses mass, which can be entirely accounted for by the charge carried. Further, Lebedew has shown that the emission of energy by matter causes a back pressure, similar to the recoil of a rifle when a bullet is fired.[4]

(2) *Energy can be localized outside matter.*—Evidence has been brought forward to show that electrons can travel freely in space, for example, as cathode rays or β-rays.

(3) *Energy is "conserved," but not mass.*—The dualistic theory supposed that the principle of the Conservation of Mass was distinct from the principle of the Conservation of Energy. But when uranium is completely converted into helium and lead, it loses one-tenthousandth of its mass, an amount which could be detected by an accurate balance in the laboratory. When 2 grams of hydrogen unite with 16 grams of oxygen to form water, about 69,000 calories of heat energy are evolved. This must involve a corresponding loss of mass, if energy possesses mass, though the change would not be measurable by ordinary methods. Thus energy must be regarded as a more fundamental thing than matter, and, in a physical or chemical

change, it is the energy and not the mass of the system which is to be regarded as conserved. Atoms of matter owe their *mass to the presence of charged units, the protons and electrons* which have figured so largely in this account of modern theories of atomic structure. Modern physical results demand the abandonment of the principle of the Conservation of Mass, and the retention of the principles of the Conservations of Energy and of Momentum.

Various theories of energy have been considered in Chapter VI. The hypothesis of light-quanta involves the idea of atoms of energy, since energy possesses mass. Radiant energy, then, possesses an atomic structure just as matter does, if this hypothesis is accepted.

With regard to the relationship existing between matter and energy, two theories are proposed, which may be termed: (1) the *Dematerialization of Matter*, and (2) the *Materialization of Energy*. According to (1), matter consists of rings or vortices in the æther. An electron, in this way, may be regarded as a kind of cavity in the æther. Empty space and æther are alone essential to the construction of the universe, which may not seem a very hopeful proposition. Theory (2) regards matter as a manifestation of energy. The latter exhibits itself to our senses in two ways. First, it appears as matter, when moving with velocities smaller than that of light, and as radiant energy when its speed equals that of light. It has been calculated, on this basis, that 1 gram of matter at rest at 0° C. has an energy equivalent of 9×10^{20} ergs, or the heat liberated by the combustion of three million kilograms of anthracite. Fantastic and sometimes horrible pictures have been drawn of the consequences of these immense supplies of energy becoming available. The utilization of atomic energy may some day provide a means of locomotion when the supplies of oil and other fuel run short. Apart from such speculations, one certain thing emerges from the discussion, namely, that energy is more fundamental in nature than matter. Matter must be explained in terms of energy.

In the foregoing, occasional reference has been made to the æther of space. The æther is postulated to explain the undulations of radiant energy. It is regarded as the medium through which wave motions are carried. Apart from the conception, it is not easy to visualize waves of definite length in empty space. The history of the ætherial medium shows that many mutually contradictory properties have, at different times, been assigned

to it. It has appeared as a fluid of low density, or as a dense solid many thousands of times as heavy as lead. The leading characteristic of the æther is its property of transmitting waves of all lengths with the same speed, a fundamental constant in physical theory, equal to about 3×10^{10} cms. per second.

Lodge has recently raised some interesting speculations which may be worthy of inclusion here.[5] The action of X-rays in producing electrons from matter is a reciprocal one, that is, the secondary β-radiation produced can cause matter to emit X-rays. Further, according to theories of radiant energy expounded in section 33, light is produced by the acceleration of an electron. Lodge asks us whether another process may not be possible in certain circumstances, namely, the formation of an electron by radiant energy. The suggestion is carried further than this, and the question is raised as to whether the immense amount of solar energy radiated into space may not sometimes generate atoms of matter.

60. The Outlook for the Future

This volume will be closed with a few general considerations, particularly in relation to the problems which await solution. It is of interest, in this connection, to place ourselves in the position of a scientist nearer the commencement of the present century, as he considered the future outlook at that time. The following words were written in 1906 by Johnstone Stoney,[6] who will be remembered as the originator of the term "electron": "The greatest achievement of all, and one to which we may reasonably look forward, has not yet been effected. No one has yet succeeded in tracing back from the periodicities, the intensities and other properties of the lines of a spectrum of an element what that motion of the electrons within the molecules must have been to have been able to produce just these precise effects. The information is given to us by nature in the spectrum exhibited to us. It is written there; but in a language which has never been deciphered." It may now be said that the Rosetta stone of this language has been discovered. The work of Bohr and his school, extended by Sommerfeld and others, has very definitely advanced the interpretation of the experimental data. A few simple assumptions can account quantitatively for the wave-numbers of the lines of the series spectra of hydrogen and singly-ionized helium. The problem of the more complex atoms requires further elucidation; the

subject is beset with great difficulties, but a beginning has been made. The values of Moseley's constants for the shielding effect of external electrons will have to be considered, and may be deduced with theoretical precision. The relationships between the optical emission spectral lines of different atoms with each other are imperfectly understood, and, considering the general similarity of the structures assigned to atoms, many further quantitative relationships would appear to await discovery. The evidence of absorption spectra must also be taken more fully into account, a beginning having been also made in this direction. The dynamic atom model may be extended to give an account of chemical combination, and to explain the optical emission spectra of molecules. So far, little has been done in the case which is presumably simplest of all, namely, the molecule of hydrogen.

Knowledge of the structures of atomic nuclei is very incomplete, as pointed out in Chapter VII.

Some reference has been made to the controversy which exists between the static and dynamic schools of thought in relation to atomic structure. There are evidently truths in each conception; the reconciliation between them must be awaited. The static theory of the atom has had some success in explaining chemical combination and the nature of valency (Chapter IX). It has given some account of the combination between atoms, radicals and compounds. All radiation phenomena, however, call for a dynamic model. The merits of each standpoint may be somewhat underestimated by members of the opposite school of thought, and satisfactory development is apparently only possible by combining the truths in the two points of view.

The problem of the transmutation of the elements, the unrealized dream of the alchemic mind, has been found to be capable of solution, in a few limited cases, in certain hard and fast conditions. Disintegration occurs in the radioactive series, where the changes are spontaneous, and, so far as definite evidence goes, is independent of any alteration in conditions which it is possible to effect. Rutherford has also disintegrated some of the lighter elements artificially. The production of hydrogen nuclei from nitrogen is a definite transmutation of an analytical type. Physicists are very far, however, from being able to produce changes in atomic structures at will, though this difficulty may yield considerably to future research.

Certain claims which have been made in this connection

may be noted here. In 1913, Collie and Patterson stated that they had produced neon by passing an electric discharge through hydrogen at low pressure.[7] Wendt and Irion (1922) claim to have obtained helium by the action of a condensed discharge upon fine tungsten wires in a vacuum.[8] Lastly, we may note the recent observation of Miethe, of the formation of gold in a mercury vapour lamp, when burning overcharged.[9] These conclusions await confirmation.

It should also be borne in mind that the miniature world of protons and electrons may not be the ultimate goal. It is at least possible that these units may have some structure of their own.

In all directions, knowledge must advance cautiously onwards. Improved apparatus and methods are available for the investigator in the atomic field. Johnstone Stoney, in the following extract, was speaking of the state of knowledge at the time of writing: "This he" (the thoughtful student) "should entertain, not like a stereotype plate which must remain as it is, but rather like well and firmly set moveable type, susceptible with ease of any improvements the future may bring with it, while before and after each correction it is so firmly fixed in its frame that the most effectual use can be made of it."[8]

It may possibly seem that much which has been discussed in this volume has little direct bearing on the world of practical affairs. Actually, however, scientific discoveries of all kinds, and particularly those relating to such fundamental matters as are here considered, ultimately affect in no small degree the social and economic life of the world. The atomic changes which yield X-rays have been used in surgery, where they are of great value. The accomplishment of broadcasting speeches and musical programmes has been rendered possible by the discovery of the thermionic valve, whose action depends upon the emission of electrons from the atoms of a heated wire. It is early, perhaps, to expect great industrial developments from the results obtained as to atomic structures, but the commencement of the twentieth century has been marked by such notable advances in experimental power that we may look with confidence to the discovery of further applications in the future. It is now possible to study, by means of the ultramicroscope, the movement of particles whose sizes are not far distant from those of molecules. The structure of a crystal can be probed, by using the planes of atoms as reflecting surfaces for X-rays. By means of the mass-spectrograph, atoms can be weighed by the

lines they produce on a photographic plate. A kind of atomic billiards with α-particles and atomic nuclei is possible, and the movements before and after impact can be watched by the cloud method. These things, to mention a few only, show how great are the advances which have been made.

It is a debatable question as to whither the new knowledge is leading us. One thing, however, would seem to be clear. Benefit can only accrue to mankind so long as development in other directions keeps pace with the advance of science.

REFERENCES : (X)

See Nos. 5 and 7 in Bibliographical List at end of book

1 (p. 270) A. W. MICHELSON and E. W. MORLEY: "On the Relative Motion of the Earth and the Luminiferous Ether"; *Amer. J. Sci.*, 1887; **34**, 333.

2 (p. 272) A. EINSTEIN: "Zur Elektrodynamik bewegter Körper"; *Ann. Physik*, 1905; (iv.) **17**, 891 : **18**, 639. See also: *Idem : Jahr. Rad. Elekt.*, 1908; **4**, 411. For references to earlier papers on relativity, see J. LAUB: *Jahr. Rad. Elekt.*, 1910; **7**, 405.

A. EINSTEIN: "Die Grundlage der allgemeinen Relativitätstheorie"; *Ann. Physik*, 1916; (iv.) **49**, 769.

Royal Society Discussion on Relativity: *Proc. Roy. Soc.*, 1920; **A97**, 66.

Relativity Symposium: *Nature*, 1921; **106**, 781.

See also No. 7 in Bibliographical List, as well as the follow- books in English:—

A. EINSTEIN: "The Meaning of Relativity"; Methuen & Co., Ltd.

A. EINSTEIN, H. A. LORENTZ, M. MINKOWSKI, and others: "The Principle of Relativity"; English translation by G. B. Jeffery and W. Perrett; Methuen & Co., Ltd.

A. S. EDDINGTON: "Space, Time and Gravitation; an Outline of the General Relativity Theory"; Cambridge University Press.

Idem: "The Mathematical Theory of Relativity"; Cambridge University Press.

J. H. THIRRING: "The Ideas of Einstein's Theory"; Methuen & Co., Ltd.

J. RICE: "Relativity: A Systematic Treatment of Einstein's Theory"; Longmans, Green & Co.

A. KOPFF: "The Mathematical Theory of Relativity"; English translation by H. Levy; Methuen & Co., Ltd.

Other works will be found in Messrs. Methuen's list.

3 (p. 274) G. N. LEWIS: "A Revision of the fundamental Laws of Matter and Energy"; *Phil. Mag.*, 1908; (vi.) **16**, 705.

L. T. MORE: "On Theories of Matter and Mass"; *Phil. Mag.*, 1909; (vi.) **18**, 17.

N. CAMPBELL: "The Æther"; *Phil. Mag.*, 1910; (vi.) **19**, 181.

P. LANGEVIN: "L'inertie de l'energie et ses consequences"; *J. Physique*, 1913; (v.) **3**, 553.
See also numerous papers by Poincaré and others.

4 (p. 274) P. LEBEDEW: "Untersuchung über die Druckkräfte des Lichtes"; *Ann. Physik*, 1901; (iv.) **6**, 433. See also E. L. NICHOLS and G. F. HULL: *ibid.*, 1903; (iv.) **12**, 228.

5 (p. 276) O. LODGE: "The Ether and Electrons"; *Nature*, 1923; **112**, 185.

6 (p. 276) G. JOHNSTONE STONEY: Introduction to "The Electron Theory," by E. E. Fournier d'Albe; 1906 (Longmans, Green & Co.).

7 (p 278). J. N. COLLIE and H. S. PATTERSON: "The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures"; *J. Chem. Soc., Trans.*, 1913; **103**, 419.

8 (p. 278) G. L. WENDT and C. E IRION: "Experimental Attempts to decompose Tungsten at high Temperatures"; *J. Amer. Chem. Soc.*, 1922; **44**, 1887.

9 (p. 278) A. MIETHE: "Der Zerfall des Quecksilberatoms"; *Naturwiss.*, 1924; **12**, 597. See also: *Idem* with H. STAMMREICH: *Z. Anorg. Chem.*, 1924; **140**, 368.

BIBLIOGRAPHICAL LIST

This list of works in English is appended by the kind permission of the various publishing houses concerned. The prices of the books are given.

1. E. RUTHERFORD: "Radioactive Substances and their Radiations"; 1st Edition, 1913. 20s. net. (University Press, Cambridge.)
2. J. S. TOWNSEND: "Electricity in Gases"; 1st Edition, 1915. 16s. net. (Clarendon Press, Oxford.)
3. J. A. CROWTHER: "Ions, Electrons, and Ionizing Radiations"; 4th Edition, 1924. 12s. 6d. net. (Edward Arnold & Co., 41 and 43 Maddox Street, W. 1.)
4. J. J. THOMSON: "Rays of Positive Electricity, and their Application to Chemical Analysis"; 2nd Edition, 1921. 16s. net. (Longmans, Green & Co., 39 Paternoster Row, E.C. 4.)
5. L. ROUGIER: "Philosophy and the New Physics"; English translation by M. Masius; 1st Edition, undated. 6s. net. (Messrs. George Routledge & Sons, Ltd., Broadway House, 68-74 Carter Lane, E.C. 4.)
6. A. S. RUSSELL: "An Introduction to the Chemistry of Radioactive Substances"; 1st Edition, 1922. 6s. net. (Mr. Murray, 50A Albemarle Street, W. 1.)
7. A. EINSTEIN: "Relativity: The Special and the General Theory"; English translation by R. W. Lawson; 7th Edition, 1922. 5s. net. (Methuen & Co., Ltd., 36 Essex Street, W.C. 2.)
8. F. W. ASTON: "Isotopes"; 2nd Edition, Revised and Enlarged, 1924. 10s. 6d. net. (Edward Arnold & Co.)
9. N. BOHR: "The Theory of Spectra and Atomic Constitution"; English translation by A. D. Udden; 1st Edition, 1922. 7s. 6d. net. (University Press, Cambridge.)
10. A. STOCK: "The Structure of Atoms"; English translation by S. Sugden; 1st Edition, 1923. 6s. net. (Methuen & Co.)
11. A. SOMMERFELD: "Atomic Structure and Spectral Lines"; English translation by H. L. Brose; 1st Edition, 1923. 32s. net. (Methuen & Co., Ltd.)
12. J. PERRIN: "Atoms"; English translation by D. Ll. Hammick; 2nd Edition. Revised and Enlarged. 1923. 8s. 6d. net. (Constable & Co., Ltd., 10-12 Orange Street, W.C. 2.)
13. H. A. KRAMERS and H. HOLST: "The Atom and the Bohr Theory of its Structure"; English translation by R. B. and Rachel T. Lindsay; 1st Edition, 1923. 10s. 6d. net. (Gyldendal, 11 Hanover Square, W. 1.)
14. E. N. DA C. ANDRADE: "The Structure of the Atom"; 2nd Edition, 1924. 16s. net. (G. Bell & Sons, Ltd., York House, Portugal Street, W.C. 2.)

15. W. H. BRAGG and W. L. BRAGG: "X-Rays and Crystal Structure"; 4th Edition, Revised and Enlarged, 1924. 21s. net. (G. Bell & Sons.)
16. N. BOHR: "On the Application of Quantum Theory to Atomic Structure. Part I. The Fundamental Postulates"; English translation (from *Z. für Phys.*, 1923; **13**, 117) by L. F. Curtiss, 1924. 3s. 6d. net. (University Press, Cambridge.)
17. J. A. CRANSTON: "The Structure of Matter"; 1st Edition, 1924. 12s. 6d. net. (Blackie & Sons, Ltd., 17 Stanhope Street, Glasgow.)
18. O. LODGE: "Atoms and Rays"; 3rd Edition, 1924. 21s. net. (Ernest Benn, Ltd., 8 Bouverie Street, E C.)
19. J. D. MAIN SMITH: "Chemistry and Atomic Structure"; 1st Edition, 1924. 12s. 6d. net. (Ernest Benn, Ltd.)
20. R. A. MILLIKAN: "The Electron"; 2nd Edition, 1924. 9s. 6d. net. (University of Chicago Press.)
21. F. REICHE: "The Quantum Theory"; English translation by H. S. Hatfield and H. L. Brose; 2nd Edition, 1923. 6s. net. (Methuen & Co.)

A list of some leading works on Relativity is given under References (X), No. 2.

INDEX OF AUTHORS

(The numbers refer to pages; those in plain type to the text, and those in heavy type to references)

ABEGG, 214, **265**.
Adam, 75, **80**.
Andrade, 95, **99**, 112, **122**, 164-5, **281**.
Aronberg, 112, **122**.
Arrhenius, 22, **39**, 149, **156**.
Astbury, 74, **79**, **80**.
Aston, 55-8, **77**, 113, 116, **122**, 159, **281**.

BAEYER, **166**.
Balmer, 172, **210**.
Barkla, 103, 105, **121**, **155**.
Barlow, 61.
Barratt, **210**.
Bartlett, **78**.
Becker, 153.
Becquerel, 81, **96**, **97**.
Begeman, 29.
Bell, **210**.
Benedicks, 138, **154**.
Bernal, **79**.
Bernouilli, 1, 5, 261.
Berzelius, 60.
Bieler, 166, **167**.
Bishop, **20**.
Bjerrum, **154**.
Blackett, 93, **98**, 110.
Blanc, **122**.
Blondlot, 59, **77**.
Bodländer, **265**.
Bodoszewski, 9.
Bohr, 18, 34, 112-3, **122**, 158, 175 *seq*., **210**, **211**, 257, 259, 262-3, **267**, **281**, **282**.
Boltwood, **98**, 111, **121**, **122**.
Boltzmann, 6.
Born, 69, **78**, 262, **268**.
Bosanquet, 262, **268**.
Bothe, **99**.
Bowen, 231, **265**.
Boyle, 1, 2.

Bozorth, **79**.
Brackett, 172-3.
Bragg, W. H., 38, **40**, 62-3, **78**, **79**, **282**.
Bragg, W. L., 62-6, **78**, **79**, 168-9, **210**, 231, 262, **266**, **268**, **282**.
Bravais, 61.
Briggs, 213, **268**.
Brockman, 252, **267**.
Broek, van den, 102, **120**.
Brönsted, 114, **122**.
Brown, 9.
Bucherer, 37, **40**, 94, **98**.
Burgess, 246, **267**.
Burton, 15, **20**.
Bury, 232, **266**.

CAMPBELL, **268**, **279**.
Cannizaro, 4, **19**.
Carbonelle, 9.
Carnot, 273-4.
Cassini, 261.
Caven, 241, **266**.
Chadwick, 109, **121**, 166, **166**, **167**.
Charles, 5.
Chwolson, 166, **167**.
Clausius, 16-7, 22
Collie, 278, **280**.
Compton, 153, **156**.
Coster, **121**, **211**, **267**.
Cranston, **282**.
Crehore, 166, **167**.
Crookes, 8, **19**, 49-51, **77**, 83-4, **97**.
Crowther, **99**, 104, **281**.
Cunningham, **19**, 33.
Curie, Mme., 81, 93, **96**, 97, **98**, 1
Curie, P., 81, 93, **96**, 97, **98**, 1
256-7, **267**.

DABROWSKI, **20**.
Dalton, 1-4.

Danysz, **186.**
Darwin, 76, **80**, 104, 119, **121**, **123**, **167.**
Dauvillier, 254.
Davey, **78**, **79.**
De Broglie, 9, 12, **20**, 34, **155**, 203-5, **211.**
Debus, **18.**
Debye, 69, **78**, **79**, **80**, 141, **155**, 262, **268.**
Demarçay, 81, **96.**
Dempster, 58, **77**, 116, **122.**
Dolejšek, **121.**
Dorn, **97.**
Duane, **155**, **156.**
Dulong, 7, 139, 141.
Dushman, 149, **156.**

Eastman, 237, 252, **266.**
Eddington, **279.**
Edlund, 237, **266.**
Ehrenfest, **122.**
Ehrenhaft, 34, **40.**
Einstein, 11-12, **19**, 136, 140-8, 151-3, **154**, **155**, 269-72, **279**, **281.**
Ellis, 94, **99**, 163-5, **167.**
Elster, 41, 111, **122**, 144.
Enright, 25, **39.**
Eucken, 137, **154.**

Fabry, 171.
Fajans, 69, **78**, 118, 120, **123**, 260, **268.**
Faraday, 22-4, **39**, 49, 126-7, **153**, 256.
Federow, von, 61.
Fitzgerald, **153.**
Fletcher, 12, **20.**
Flürscheim, 242-3, **266.**
Foote, 202, **211.**
Föppl, 221.
Foucault, 124.
Fowler, **77**, **210**, 229, **265.**
Franck, 147, **155**, 202, **211.**
Frankenheim, 61.
Fresnel, 130.
Friedrich, 61, **78.**

Gay Lussac, 3-4, **18.**
Geiger, **34**, 90-1, **97**, **98**, **99**, 104-5, **121.**
Geitel, **41**, 111, **122**, 144.
Giesel, **97.**
Goldstein, 53.
Gouy, 9, **19.**
Grindley, **79**, **80.**
Groth, von, 60.
Grüneisen, **154.**
Guglielmini, 59-60.
Guldberg, 5, **19.**

Hahn, 111, **121**, **166.**
Hallwachs, 144, **155.**
Hantzsch, 247, **267.**
Harkins, **98**, 112, **122**, 162, **166.**
Harrington, 34.
Hartree, **265.**
Haüy, 59-60.
Hedges, **20.**
Helmholtz, 23, **39.**
Henri, **79.**
Henry, 2.
Henstock, 245, **267.**
Hertz, G., 147, 202, **211.**
Hertz, H., 100, 125, 128, 144, **153**, **155.**
Herzfeld, 38, **40.**
Hevesy, von, 114, **121**, **122**, **123.**
Holst, **281.**
Hull, A. W., **79**, **80**, 229, **265.**
Hull, G. F., **280.**
Hunt, **155.**
Hyman, 111-2, **122.**

Iklé, 96, **99.**
Ingold, **154.**
Irion, 278, **280.**

Jahnke, 131.
James, 262, **268.**
Johnstone Stoney, 23-4, **39**, 59, **77**, 276, 278, **280.**
Joule, 16.

Kaufmann, 37, 52, 94, **98.**
Kaye, 106.
Keetman, 111, **121.**
Kermack, 243, **267.**
Kinoshita, **121.**
Kirchoff, 130, 131.
Knipping, 61, **78.**
Knorr, 260, 262, **268.**
Kohlweiler, 114, **122.**
Kopff, **279.**
Kossel, 203, **211**, 214, 218-21, 238-9, 262, **265.**
Kramers, **281.**
Kratzer, 113, **122.**
Kroo, **268.**
Kurlbaum, 131, **154.**
Kuss, **266.**

LADENBURG, **154.**
Landé, 69, **78**, 262, **268.**
Lang, von, 60.
Langevin, **19**, 44-5, **76**, **77**, 256-7, **267**, **280.**
Langley, 132, **154.**
Langmuir, 75, **78**, **80**, 158, **211**, 222 *seq.*, 259, 263, **265**, **266**, **268.**
Lantsberry, **98.**
Laplace, 25.
Lapworth, 243-5, **266**, **267.**
László, **79.**
Latimer, 246, **267.**
Laub, **279.**
Laue, *61-2*, **78.**
Laurie, 263, **268.**
Lavoisier, 25.
Lebedew, 50, 274, **280.**
Le Bel, 70-1.
Lenard, 50, **77**, 144-6, **155.**
Lewis, G. N., 158, 212 *seq.*, 239, 259, **264**, **279.**
Lewis, W. C. M., 149, **156.**
Lindemann, 141-2, **155.**
Linss, 41.
Livens, *181*, **210.**
Lockyer, 89.
Lodge, 25, 105, **121**, 182, **210**, 276, **280**, **282.**
Loeb, **77.**
Loomis, 113, **122.**
Lorentz, 94, **156**, **279.**
Lowry, **19**, 224, 232-42, 246-7, 249, 255, **265**, **266**, **267.**
Lucretius, 1.
Lummer, 131, 133-4, **154.**
Lyman, 172-3.

MAIN SMITH, 247, 254-5, **267**, **282.**
Marcelin, 149, **156.**
Marckwald, 111, **121.**
Marsden, 90-3, **98**, 104-5, **121.**
Marsh, **210.**
Maxwell, 6, 8, 16-17, **19**, 23-4, 129-30, **154.**
Mayer, *168.*
McKeown, **156.**
McLennan, **155**, **265.**
Meisenheimer, 233.
Meitner, 94, **98**, **99**, 117, 120, **123**, 161-2, **166**, **167.**
Merton, 112, **122**, **210.**
Meyer, 87, **97.**
Michelson, 171, **210**, 269-70, **279.**
Miethe, 278, **280.**
Millikan, 9, **20**, 29 *seq.*, **39**, **40**, 145, **155**, **156**, 206, **211**, 231, **265**, **282.**
Minkowski, 270, **279.**
Mitscherlich, 60.
More, **279.**
Moreau, 34.
Morgan, 247, 255, 260-1, **267**, **268.**
Morley, 4, **19**, 269-70, **279.**
Moseley, 106-9, 111, 118, **121**, 170-1, 185-6.
Müller, 74-5, **80.**

NERNST, 141, **155.**
Neuburger, 117, **122.**
Newton, *1*, *124*, *269*, *271-2.*
Nichols, **280.**
Nicholson, 253.
Nicol, **121.**
Noddack, 148, **156.**
Norrish, 148, **156**, 237, **266.**
Nuttall, 105, **121.**

OSTWALD, 13.
Oxley, 258-60, **268.**

PANETH, **122.**
Pascal, 260.
Paschen, **154**, 172-3, 229, **265.**
Pasteur, 74.
Patterson, 278, **280.**
Pauli, 257, **267.**
Perot, 171.
Perrin, 9, 12, 13-15, 17, **19**, **20**, 34, 51, **77**, 148-9, **156**, **281.**
Petit, 7, 139, 141.
Pier, 7, 137, **154.**
Piper, 75, **80.**
Pirogoff, 6.
Planck, 6, 34, 131, 133-5, 140, 152, **154**, 180-1, 188.
Pohl, 59, **78.**
Poincaré, 152, **156**, **280.**
Porter, 15, **20.**
Posnjak, **79.**
Prideaux, 234, **266.**
Priess, **266.**
Pringsheim, 131, 133-4, **154.**
Prout, 4, 55, 58.

RAMSAY, 9, **39**, 89, **97**, **98.**
Rankine, 226-7, **265.**
Ratner, 53, **77.**
Rawlinson, **99**, **167.**
Rayleigh, 130, 132, 134-5, **154.**
Regener, 34, 88-9, **97.**

Reiche, **282**.
Rice, 149, 153, **156**, **279**.
Richards, 112, **122**.
Richardson, **120**.
Rideal, 148, **156**.
Ritz, 173.
Roberts-Austen, **19**.
Robinson, H., **99**, **167**, **211**.
Robinson, R., 237, 243, **266**, 267.
Rodebush, 246, **267**.
Röntgen, 58, **77**, 81.
Rossi, 112, **122**.
Rougier, **281**.
Royds, **97**.
Rubens, **154**.
Rubinowicz, 205, **211**.
Russell, 112, **122**, **123**, **281**.
Rutherford, 34, 41-4, **76**, 85, 89-92, 95-6, **96**, **97**, **98**, **99**, 104-5, 112, **121**, **122**, 159-61, 163-6, **166**, **167**, **281**.
Ryan, **98**.
Rydberg, 170, 172, 174, 222, **265**.

Scherrer, 13, **20**, 69, **78**, **79**, **80**.
Schonflies, 61.
Schonland, **99**.
Schott, 181, **210**.
Schrödinger, 143, **155**.
Schuster, **77**.
Seddig, 12, **19**.
Semenow, 59, **78**.
Shearer, 74-5, **80**.
Shoesmith, 244-5, **267**.
Sidgwick, 250-4, **267**.
Siedentopf, 9, **19**.
Siegbahn, 112, **121**, **122**, **210**.
Simon, 80.
Simson, 80.
Skinner, **167**.
Smith, 227, 229, **265**.
Smoluchowski, 8-9, 11, **19**.
Smythe, 153.
Soddy, 85, 89, **97**, 111-2, 118-9, **121**, **122**, **123**.
Sohncke, 61.
Sommerfeld, **78**, 189 *seq.*, **210**, 257-8, [illegible], **281**.
Spiers, 252, **267**.
Stammreich, **280**.
Stark, [illegible].
Stenström, 112, **122**.
Stewart, A. W., 114, **122**, **210**.
Stewart, [illegible] D., 237, **266**.
Stock, [illegible], **281**.
Stokes, 59, **77**, 129.
Stoletow, 144.
Stoner, 254, 258, **267**, **268**.
Strutt, **96**, **123**.
Sugden, 238, **266**.
Svedberg, 12, **19**.

Tate, 202, **211**.
Thirring, **279**.
Thompson, 81, **96**.
Thomson, **19**, 27, 37-8, **39**, **40**, 41-2, 51-6, **76**, **77**, **98**, **99**, 105, **121**, 129-30, 144, 152, **154**, **155**, **156**, 168, **210**, 212, 220-2, 234, **264**, **265**, **281**.
Townsend, 24-7, **39**, 42-7, **77**, **281**.
Trautz, 149, **156**.
Trouton, 128, **153**.
Tutton, **78**.
Tyndall, 9, **19**.

Usherwood, **154**.

Van't Hoff, 70-1, 238.
Vegard, **78**, **79**.
Vleck, van, **211**.

Waage, 5, **19**.
Wadsworth, 112, **122**.
Wagner, 147, **155**, **210**.
Walter, 59, **78**.
Watson, 153.
Webster, 147, **155**.
Weiss, 256-7, **267**.
Wellisch, 47, **77**.
Welsbach, von, 111, **121**.
Wendt, 278, **280**.
Werner, 239, 247-8, 253.
Whittaker, 260, **268**.
Whytlaw Gray, 89-90, **98**.
Wick, **79**.
Wiechert, 51.
Wien, 53, **77**, 131-2, 134-5, **154**.
Wilsey, **78**.
Wilson, C. T. R., 27, **39**, 41, **76**, 90-1, 94-5, **98**, **99**.
Wilson, H. A., 27-9, **39**.
Wilson, W., 192, **210**.
Wood, 149, **156**.
Wyckoff, **78**, **79**, 232, **266**.

Yardley, **80**.

Zeleny, 44, **78**.
Zsigmondy, 9, 13, **19**.

INDEX OF SUBJECTS

(*The numbers refer to pages*)

ABEGG'S —, 214-5.
Absorption bands, edges of, 146-7, 203-5.
Acetic acid, structure of, 224-5, 242, 247.
Acetylacetone compounds, 248-9.
Acids, definition of, 239.
Action, Planck's quantum of, 134-5, 145-7, 180.
— unit of, 188-9.
Æther, the, 23, 125-6, 275-6.
Affinity, chemical, transmission in chains, 242-5.
— residual, 246-8.
Agglomeration theory, 138.
Aliphatic compounds, X-ray spectra of, 74-5.
Alternate induced polarities, effect of, 242-5.
Aluminium, specific heat of, 141-2.
Alpha particles, charges of, 89.
— — effects of, passing through matter, 90-2, 100-1, 159-61.
— — *e/m* ratio for, 88.
— — identical with helium nuclei, 89, 92.
— — mass of, 89, 159.
— — neutralized, in nuclei, 117, 120, 161-2.
— — size of, 110.
— — shape of, 110, 166.
— — tracks of, 90-2.
— — velocities of, 88.
Alpha rays, 82, 87 *seq.*
— — scattering of, by gases, 92-3, 105, 159-61.
— — — — by metal foils, 90-2, 104-5, 109.
Angular momentum, 179-80, 183, 187, 190-1.
— velocity, 179, 183, 187.
Anticathode, 58.
Arc spectra, 172-4.
Atomic diameter, definition of, 16.
— — determination of, 16, 17.
Atomic heat of argon, 7, 137, 150.
Atomic kernel, 214.
Atomic models, Bohr's, 175 *seq.*
— — Bury's, 232.
— — Langmuir's, 222 *seq.*
— — Lewis', 213 *seq.*
— — Thomson's, 168, 220.
— — types of, 157-8.
Atomic nature of electricity, 23 *seq.*
Atomic nuclei, 92, 100-1.
— — as dipolar spheres, 245.
— — charges of, 103-9, 115.
— — energy levels in radioactive, 164-5.
— — masses of, 92, 109, 115.
— — negative electrons in, 109, 115-7.
— — parts of, 159-62.
— — sizes of, 109-11, 150-1.
— — stability of, 118.
— — structure of, 165-6.
Atomic number, definition of, 102.
— — significance of, 102-11, 119.
Atomic sheath, 214.
Atomic shells, 222-3.
Atomic weights, 3.
Atoms, absolute mass of, 5, 13-14.
— Dalton's theory of, 1-3.
— high frequency spectra of, 106-9, 112-3.
— optical spectra of, 108, 112, 172-4, 200-1, 207, 209.
Avogadro number, 4, 13-5, 34, 136.
— hypothesis of, 4-5, 15.

BALMER series, 172, 175-6.
Bases, definition of, 239.
Beta rays, 82, 93-5.
— — *e/m* ratio for particles of, 94.

Beta rays, origin of, 94, 163.
— — tracks of, 94-5.
— — velocities of, 94.
Black body, 6, 130-1.
Bohr theory, of line spectra, 175 *seq*.
— — general, of atomic structure, 205-9.
Bolometer, 132.
Boyle's law, 1, 5.
Brownian movement, 8 *seq*.

CALCITE, crystalline structure of, 72.
Carbonyls, 249.
Carnot's principle, 273-4.
Cassinian ovals, 261.
Cathode rays, 50-3.
Characteristic X-rays, 59, 103, 106-9.
Charles' law, 5.
Chelate groups, 255.
Chemical affinity, transmission in chains, 242-5.
Circular orbits (Hydrogen), 176, 186-9.
— — — energy associated with, 177-9, 182-3, 188.
— — — periodic times of, 187, 194-5.
— — — radii of, 186.
Cluster theory, 47.
Colloidal solutions, 9, 14.
Combination relationships, 164-5, 169, 173-5.
Comolecules, 227.
Compounds, 2.
— complete and incomplete, 224-5.
— spectra of, 171.
— structures of, 212 *seq*.
Constitutive properties of atoms, 221.
Contravalency, 215.
Co-ordination, centric and cyclic, 255.
— chelate, 255.
— numbers, 248-9, 252-4.
— Sidgwick's rule concerning, 253-4.
— valency of radicals in, 248, 250-1.
Correspondence principle, 205.
Covalency, 224.
Crossed polarities, 255.
Crystallography, principles of, 59-63.
Crystal structure, data for inorganic crystals, 65-72.
— — — — organic crystals, 72-6.
— — determination of (Braggs), 62 *seq*.
— — — — (Hull), 76.
— — — — (Laue), 61-2.

DALTON'S Atomic Theory, 1-3.
Degrees of freedom, 6-7, 136-40.
Delta rays, 95.
Dependence of reaction velocity on temperature, 149.
Diamagnetism, 256.
Diamond, crystal structure of, 67, 70-1.
— specific heat of, 141-3.
Differential Calculus, applicability of, 272-3.
Diffusion coefficient, 42, 45-6.
Disintegration, artificial, 159-62.
— radioactive, 81 *seq*.
Double bond, explanation of, in octet theory, 217.
Duplets, 223.

EFFECTIVE atomic numbers, 250-1.
— — — of complex compounds, 252-3, 255.
Electric discharge in gases, 49-50.
Electricity, atomic nature of, 23 *seq*.
Electrolysis, 21-3.
Electromagnetic mass, 36-8, 94, 274.
— theory of light, 129-30.
— waves, 59, 125-30.
Electronic charge, evaluation of (Millikan), 29-35.
— — — — (Planck), 136.
— — — — (Rutherford), 34, 88-9.
— — — — (Thomson), 27.
— — — — (Townsend), 25-7.
— — — — (Wilson), 27-9.
Electronic theory of valency, 214 *seq*.
— — — — conclusions of, 264.
Electrons, 23, 36-9.
— angular velocity of, 179, 183, 187.
— distribution of, among sub-groups, 208, 254-5, 258.
— effective mass of, 177-8.
— e/m ratio for negative, 36-7, 51-2.
— in matter, evidence for existence of, 49, 53, 94, 100-1.
— lone pairs of, 239.
— vibrations of, 129, 135-6.
Electrovalency, 224.
Element, definition of, 2, 117-8.
Elementary chaos, 6.
Elements, high frequency spectra of, 106-9.
— periodic classification of, 17-18, 118-20, 205-9, 214 *seq*.
— transmutation of, 85, 277-8.
Elliptic orbits (Hydrogen), 189 *seq*.

Elliptic orbits (Hydrogen), eccentricity of, 193.
— — — energy of, 192-3, 198.
— — — geometrical properties of, 193-7.
— — — precession of, 198-9.
Energy, distribution of, among wave-lengths, 131-5.
— dualistic theory of, 274.
— electronic, in orbit, 177-8.
— mass of, 270-1, 274.
Entropy, 6.
Equipartition law, 6-7, 136-40.
Errors, law of, 6.

FERRO-MAGNETISM, 256.
Fine structure of hydrogen lines, 189-90, 196, 198-200.
Fluorine molecule, octet structure of, 216-7.
Fluorspar, crystal structure of, 67, 70.
Freedom, degrees of, 6-7, 136-40.
Free valencies, 247.
Frequency of atomic vibrations, 141-2.
Frictional electrification, nature of, 127.

GAMMA rays, 82, 95.
Gas equation, 5.
— ions, 25-30, 41-9.
Gaseous conduction, 41-9.
Gases, liquefaction of, 8-9.
— mean free path in, 16-17.
— — molecular speeds in, 16.
— viscosity of, 16-17.
General effect of substitution in organic compounds, 241-2.
— theory of atomic structure (Bohr), 205-9.
— — — relativity, 271-2.
Graphite, crystal structure of, 72.
Gravitation, theory of, 271.
Group displacement law, 118-9.

HAFNIUM, discovery of, 108.
Haüy's crystal theory, 59-60.
Helium, ionized, optical line spectra of, 173.
Hertz's radiation experiments, 128.
Hetero- and homopolarity, 212.
Heterobares and heterotopes, 117.
High frequency spectra of elements, 106-9.
Hydrogen, molecular heat of, 137-9.
— optical spectra of, 172-5.
Hydrogen, structure of (Bohr175), *seq.*
— valency of, 246.

ICE, crystal structure of, 71-2.
Induction, 126-8.
Intrinsic properties of atoms, 221.
Ionic mobility in gases, 42.
— — — — determination of (Langevin), 44-5.
— — — — — — (Rutherford), 43-4.
— — — — effect of pressure on, 47-8.
Ionic molecules, 212.
Ionization frequency, 188-9.
— in gases, mechanism of, 41-9.
— — solution, theory of, 22-3.
— intramolecular, theory of, 130, 212-3, 232-8.
— of acids and bases, mechanism of, 239-40.
— potential, 188, 201.
— wave-length, 189.
Ionized and non-ionized linkages, 260 *seq.*
Ions in gases, charges of, 24-5.
— — — produced by cathode rays, 95, 146.
— — — radium rays, 27, 81-3, 146.
— — — ultraviolet light, 27, 144-6.
— — — X-rays, 27, 41-6, 59, 146.
Isobares, 95, 114-8.
Isobaric isotopes, 117.
Isomerism, nuclear, 117.
Isomorphism, 60, 229.
Isosteres, 227, 229.
Isothermal equilibrium, 131.
Isotopes, 55-8, 111-8.
— classes of, 117.
— separation of, 114.
— spectra of, 112-3, 115.

K-RAYS, 103, 106-8, 169-70.
Key atoms, 243.
Kinetic theory of gases, 5-13, 15-17.

L-RAYS, 103, 106-8, 169-70.
Law of atomic diameters, 168-9, 231-2.
— — Boyle, 1, 5.
— — Charles, 5.
— — *combining volumes*, 3, 4.
— — conservation of energy, 274-5.
— — — — mass, 274-5.
— — constant composition, 3.

Law of Dulong and Petit, 7, 139, 141.
— — equipartition of energy, 6-7, 136-9.
— — errors, 6.
— — force (Thomson's), 221.
— — group displacement, 118-20.
— — inverse square, 110, 158, 165, 180, 201.
— — mass action, 5.
— — multiple proportions, 2-3.
— — photochemical equivalence, 147-8.
— — photoelectric effect, 145.
— — radiation (Planck), 135.
— — — (Rayleigh), 132.
— — — (Wien), 132.
— — rational indices, 59-60.
— — Stokes, 11-12, 25 *seq.*
— — velocity distribution among molecules, 6, 8, 132, 140, 149.
Lead, specific heat of, 141-3.
Levels of extranuclear electrons, 168-70, 204-7, 254-5, 258.
— within radioactive nuclei, 162-5.
Light, corpuscular theory of, 124-5.
— interference of, 124-5, 145, 152.
— quantum theory of, 134 *seq.*
— wave theory of, 125-6, 129-30. (See also Radiation.)
Light-quanta, 136, 143-7, 153.
Line spectra, 172 *seq.*
Linear oscillators, 135-6.
Lines of force, 126-7.
Linkages, ionized and non-ionized, 260 *seq.*
— types of, 262.
Lithium fluoride, octet structure of, 216.

M-RAYS, 103, 169-70.
Magnetic susceptibilities, 256.
— — of nitric oxide and oxygen, 257.
— — — organic compounds, 260.
Magnetic velocity line spectra, 162-5.
Magnetism, theory of (Langevin), 256.
— — (Oxley), 258-60.
— — (Weiss), 256-7.
Magneton numbers, 257-8.
Magneton (Bohr), 257.
— (Weiss), 257.
Mass of atoms, absolute, 5, 13-14, 34.
— of energy, 270-1, 274.
Mass-spectrograph, 56-7.
Matter and energy, relation between, 36, 275.
Mean free path in gases, 16, 33.
Mean molecular speeds in gases, 16-17.
Mechanism of chemical reaction, 148-50.
Mercury, orbital motion of, 198, 272.
Metals, crystal structure of, 71.
Michelson-Morley experiment, 269-70
Micrometer, network, 9.
Mixed bonds, 233.
Molecular theory, 4.
Molecules, 3-13, 15-17.
Moment of momentum, 179.
Monomolecular reactions, 5-6, 148-9.
Morphotropy, 60.
Multiple scattering of alpha rays, 90.

N-RAYS, 103, 169.
Naphthalene, crystal structure of, 73.
Nitrogen molecule, octet structure of, 225-6.
— — Kossel's structure for, 220.
Nuclear isomerism, 117.

OCTET theories, 215 *seq.*
Octets, stability of, 243.
Optical activity and crystal structure, 74.
Orbital precession, 198-9.
— — of Mercury, 198, 272.
Orbits, spatial, 263.
Organic acids, effect of halogen substitution, 241-2.
Oxygen molecule, octet structure of, 217.

PARAMAGNETISM, 256.
Period of average life, 85-6.
Periodic system of the elements, 17-18, 111-2, 114, 118-20, 168, 205-8, 214-5.
Petalons, 166.
Phosphorescence, 144, 146.
Photochemical reactions, 147-50.
Photoelectric effect, verification of Einstein's law of, 145.
Photo-electrons, 144-6.
Polarities, alternating, 242-5.
— crossed, 255.
Postulates of Bohr's theory, 180.
— — Langmuir's theory, 223.
— — Lewis' theory, 214-8.

Powder method of investigating crystal structure, 76.
Principal valencies, 215.
Principle, Carnot's, 273-4.
Probability, use of, 6, 135.
Proton, 36-8.
Prout's hypothesis, 55.

Quant theory, 143 *seq*., 153.
Quantization, space, 257-8.
Quantum mechanism (Whittaker), 260.
Quantum numbers, 180.
— — azimuthal, 191.
— — inner, 257.
— — radial, 192.
— — total, 192.
Quantum of action (Planck), 134-5, 145.
Quantum theory, 134-52.

Radial momentum, 191-2.
Radiant energy, nature of, 124-6, 152-3.
Radiation, Hertz's experiments on, 128.
— hypothesis of chemical reaction, 5-6, 148-50.
— pressure of, 8, 50, 274.
Radioactive chains, 84, 119-20.
— constants, 85-7.
— elements and periodic classification, 111-2, 114, 118-20.
— equilibrium, 85-7.
— period of average life, 85-6.
Radioactivity, an atomic phenomenon, 85.
— Crookes' experiments on, 83-4.
— discovery of, 81.
— quantitative study of, 82-3.
Radiometer (Crookes'), 8.
Radium, 81-2.
Rays, cathode, 50-3.
— Lenard, 50-1.
— positive, 53-5.
— secondary beta, 59, 163. (See also X-rays, K- L- M- and N-rays, α- β- γ- and δ-rays.)
Reactions, monomolecular, 5-6, 148-9.
Relativity, theory of, 36-7, 94, 159, 269-72.
Residual affinity, 246-8.
Resonance potential, 201-2.
Rest-mass, 271.
Rock salt, crystal structure of, 65-9.
Rydberg Constant, 172-3, 185.
Rydberg Number, 189.

Screening effects, 108-9, 171, 200-1, 277.
Secondary beta rays, 59, 163.
— X-rays, 59, 103, 105-9.
Selection principles, 205.
Sextets in atomic structure, 236.
Sharing of electrons, 216-7, 223 *seq*.
Single scattering of alpha rays, 90-2.
Solutions, colloidal, 9, 14.
— ionic theory of, 22.
Space quantization, 257-8.
Space-time continuum, 270.
Spark spectra, 174.
Spatial orbits, 263.
Special theory of relativity, 270-1.
Specific heats of gases, 136-40.
— — — *solids*, 140-2.
Spectra, atomic, 174, 200, 207, 209.
— of hydrogen, 172.
— — ionized helium, 173.
— — neutral helium, 174, 206.
Stability of hydrides, Kossel's theory of, 219-20.
Static and dynamic theories, relation between, 277.
Stationary orbits, 180.
Stokes' law, 11 *seq*.
— correction of, 33.
Sub-electrons, 36.
Sub-groups of electrons, 205-8, 254-5, 258.
Supplementary valencies, 247.

Theory, Avogadro's, 4-5.
— Bohr's, 175 *seq*.
— dematerialization of matter, 275.
— dualistic, of energy, 274.
— electronic, of valency, 214 *seq*.
— gaseous conduction, 47-9.
— gravitation, 271.
— intramolecular ionization, 232-8.
— *ionization* in solution, 21-3, 239-41.
— Langmuir's, 222 *seq*.
— lattice, of crystals, 61, 63.
— Lewis', 214 *seq*.
— light-quantum, 143 *seq*.
— magnetic, 256 *seq*.
— materialization of energy, 275.
— molecular-kinetic, 4-13, 15-17.
— Prout's, 55.
— quantum, 134 *seq*., 180.
— radiant energy, 124-6.

Theory, radiation, 5-6, 148-50.
— relativity, 269-72.
— wave, of light, 125.
Thermodynamics, applicability of, 273-4.
Thorium nucleus, composition of, 161.
Time of half-change of radiocative substance, 85-6.
Transition elements, 206 *seq.*, 232.
Transmutation of elements, 85, 277-8.
Triple bond, explanation of, 218.
Twisted octet atom, 221-2.
Types of cubic crystals, 69-70.

ULTRAMICROSCOPE, 9-10.

VALENCY, electronic theory of, 214 *seq.*
— electrons, 22-4, 119, 201, 214.
— free and supplementary, 247.
— of complex co-ordinated radicals, 248, 250-1.
— — hydrogen, 246.

Variation of specific heats with temperature, 136-43.
Viscosity of gases, 16-17.

WAVE-NUMBERS, definition of, 126.
— determination of, 171-2.
— of lines of H and He$^+$, 172-3.
Wave theory of light, 125.

X-RAY spectra of compounds, 74-5, 171.
X-rays, 41, 50, 58-9, 81, 125.
— and crystal structure, 59-76.
— characteristic, 59, 103, 106-9, 169-71.
— diffraction of, by crystals, 61-5.
— frequency of, 107, 164.
— *ionization* in gases by, 27, 41-6, 59.
— scattered, 59, 103, 105.
— wave-length of, 68, 126.
— wave-number of, 170.

ZINC blende, crystal structure of, 62, 70.

1624
LIBRARY

PRINTED IN GREAT BRITAIN AT THE UNIVERSITY PRESS, ABERDEEN

METHUEN'S GENERAL LITERATURE

A SELECTION OF

MESSRS. METHUEN'S PUBLICATIONS

This Catalogue contains only a selection of the more important books published by Messrs. Methuen. A complete catalogue of their publications may be obtained on application.

PART I. GENERAL LITERATURE

Anstey (F.)
THE LAST LOAD. *Fcap 8vo.* 5*s. net.*

Armstrong (W. W.)
THE ART OF CRICKET. *Crown 8vo.* 3*s. net.*

Bain (F. W.)
A DIGIT OF THE MOON. THE DESCENT OF THE SUN. A HEIFER OF THE DAWN. IN THE GREAT GOD'S HAIR. A DRAUGHT OF THE BLUE. AN ESSENCE OF THE DUSK. AN INCARNATION OF THE SNOW. A MINE OF FAULTS. THE ASHES OF A GOD. BUBBLES OF THE FOAM. A SYRUP OF THE BEES. THE LIVERY OF EVE. THE SUBSTANCE OF A DREAM. *All Fcap. 8vo.* 5*s. net.* AN ECHO OF THE SPHERES. *Wide Demy 8vo.* 10*s.* 6*d. net.*

Baker (C. H. Collins)
CROME. Illustrated. *Quarto.* £5 5*s. net.*

Balfour (Sir Graham)
THE LIFE OF ROBERT LOUIS STEVENSON. *Twentieth Edition. In one Volume. Cr. 8vo. Buckram,* 7*s.* 6*d. net.*

Belloc (Hilaire)
PARIS. THE PYRENEES. *Each* 8*s.* 6*d. net.* ON NOTHING. HILLS AND THE SEA. ON SOMETHING. FIRST AND LAST. THIS AND THAT AND THE OTHER. ON. *Each* 3*s.* 6*d. net.* ON EVERYTHING. ON ANYTHING. *Each* 6*s. net.* MARIE ANTOINETTE. 18*s. net.* A HISTORY OF ENGLAND. In 4 vols. Vol. I, to 1066 15*s.* net.

Birmingham (George A.)
A WAYFARER IN HUNGARY. Illustrated. *Crown 8vo.* 8*s.* 6*d. net.*

Bowen (Frank C.)
THE KING'S NAVY. Illustrated. *Fcap. 4to.* 7*s.* 6*d. net.*

Brinton (Selwyn)
THE GOLDEN AGE OF THE MEDICI. Illustrated. *Demy 8vo.* 15*s. net.*

Bulley (M. H.)
ART AND COUNTERFEIT. Illustrated. *Demy 4to.* 15*s. net.*

Campbell (Olwen Ward)
SHELLEY AND THE UNROMANTICS. Illustrated. *Second Edition, Revised. Demy 8vo.* 16*s. net.*

Chandler (Arthur), D.D., late Lord Bishop of Bloemfontein
ARA CŒLI. 5*s. net.* FAITH AND EXPERIENCE. 5*s. net.* THE CULT OF THE PASSING MOMENT. 6*s. net.* THE ENGLISH CHURCH AND REUNION. 5*s. net.* SCALA MUNDI. 4*s.* 6*d. net.*

Chesterton (G. K.)
THE BALLAD OF THE WHITE HORSE. ALL THINGS CONSIDERED. TREMENDOUS TRIFLES. CHARLES DICKENS. *All Fcap. 8vo.* 3*s.* 6*d. net.* FANCIES VERSUS FADS. ALARMS AND DISCURSIONS. A MISCELLANY OF MEN. THE USES OF DIVERSITY. *All Fcap. 8vo.* 6*s. net.* WINE, WATER, AND SONG. *Fcap. 8vo.* 1*s.* 6*d. net.*

Clutton-Brock (A.)
WHAT IS THE KINGDOM OF HEAVEN? ESSAYS ON ART. SHAKESPEARE'S HAMLET. *Each* 5*s. net.* ESSAYS ON BOOKS. MORE ESSAYS ON BOOKS. ESSAYS ON LIFE. *Each* 6*s. net.* SHELLEY, THE MAN AND THE POET. 7*s.* 6*d. net.*

Cowling (George H.)
A PREFACE TO SHAKESPEARE. Illustrated. *Crown 8vo.* 5*s. net.*

Dark (Sidney) and Grey (Rowland)
W. S. GILBERT: HIS LIFE AND LETTERS. *Second Edition. Demy 8vo.* 15*s. net.*

Dolls' House (The Queen's)
THE BOOK OF THE QUEEN'S DOLLS' HOUSE. Vol. I. THE HOUSE, Edited by A. C. BENSON, C.V.O., and Sir LAWRENCE WEAVER, K.B.E. Vol. II. THE LIBRARY, Edited by E. V. LUCAS. Profusely Illustrated. A Limited Edition. *Crown 4to.* £6 6*s. net.*

EVERYBODY'S BOOK OF THE QUEEN'S DOLLS' HOUSE. An abridged edition of the above. *Illustrated. Crown 4to.* 5*s. net.*

Edwardes (Tickner)
THE LORE OF THE HONEYBEE. *Thirteenth Edition. Crown 8vo.* 7*s.* 6*d. net.* BEEKEEPING FOR ALL. *Crown 8vo.* 3*s.* 6*d. net.* THE BEE-MASTER OF WARRILOW. *Third Edition. Crown 8vo.* 7*s.* 6*d. net.* All Illustrated. BEE-KEEPING DO'S AND DON'TS. *Fcap. 8vo.* 2*s.* 6*d. net.*

Einstein (Albert)
RELATIVITY: THE SPECIAL AND GENERAL THEORY. *Crown 8vo.* 5*s. net.* SIDELIGHTS ON RELATIVITY. *Crown 8vo.* 3*s.* 6*d. net.* THE MEANING OF RELATIVITY. *Crown 8vo.* 5*s. net.*

Other books on the **Einstein Theory**
AN INTRODUCTION TO THE THEORY OF RELATIVITY. By LYNDON BOLTON. *Crown 8vo.* 5*s. net.*

THE PRINCIPLE OF RELATIVITY. By A. EINSTEIN, H. A. LORENTZ, H. MINKOWSKI and H. WEYL. With Notes by A. SOMMERFELD. *Demy 8vo.* 12*s.* 6*d. net.*

Write for Complete Lists

Fitzgerald (Edward)
THE RUBA'IYAT OF OMAR KHAYYAM. Illustrated by EDMUND J. SULLIVAN. *Wide Crown 8vo.* 10*s.* 6*d. net.*

Forrest (H. Edward)
THE OLD HOUSES OF STRATFORD-UPON-AVON. Illustrated. *Crown 8vo.* 7*s.* 6*d. net. Also an edition limited to* 250 copies, *Fcap. 4to.* 21*s. net.*

Fyleman (Rose)
FAIRIES AND CHIMNEYS. THE FAIRY GREEN. THE FAIRY FLUTE. THE RAINBOW CAT. EIGHT LITTLE PLAYS FOR CHILDREN. FORTY GOOD-NIGHT TALES. FAIRIES AND FRIENDS. THE ADVENTURE CLUB. *Each* 3*s.* 6*d. net.* A SMALL CRUSE, 4*s.* 6*d. net.* THE ROSE FYLEMAN FAIRY BOOK. Illustrated. *Crown 4to.* 10*s.* 6*d. net.*

Gibbon (Edward)
THE DECLINE AND FALL OF THE ROMAN EMPIRE. With Notes, Appendixes, and Maps, by J. B. BURY. Illustrated. Seven volumes. *Demy 8vo.* 15*s. net* each volume. Also, unillustrated. *Crown 8vo.* 7*s.* 6*d. net* each volume.

Glover (T. R.)
THE CONFLICT OF RELIGIONS IN THE EARLY ROMAN EMPIRE. POETS AND PURITANS. FROM PERICLES TO PHILIP. VIRGIL. *Each* 10*s.* 6*d. net.*

Gotch (J. A.)
OLD ENGLISH HOUSES. Illustrated. *Demy 8vo.* 16*s. net.* Also an edition limited to 50 copies, £2 2*s. net.*

Graham (Harry)
THE WORLD WE LAUGH IN: More Deportmental Ditties. Illustrated by "FISH." *Fifth Edition. Fcap.* 8vo. 5s. *net.*

Grahame (Kenneth)
THE WIND IN THE WILLOWS. *Seventeenth Edition. Crown* 8vo. 7s. 6d. *net.* Also, Illustrated by NANCY BARNHART. *Small* 4to. 10s. 6d. *net.*

Hadfield (J. A.)
PSYCHOLOGY AND MORALS. *Sixth Edition. Crown* 8vo. 6s. *net.*

Hall (H. R.)
THE ANCIENT HISTORY OF THE NEAR EAST. *Sixth Edition, Revised. Demy* 8vo. £1 1s. *net.*

Hamer (Sir W. H.), and Hutt (C. W.)
A MANUAL OF HYGIENE. Illustrated. *Demy* 8vo. £1 10s. *net.*

Hays (Mary)
THE LOVE LETTERS OF MARY HAYS. Edited by A. F. WEDD. *Demy* 8vo. 12s. 6d. *net.*

Hewlett (Maurice)
THE LETTERS OF MAURICE HEWLETT. Edited by LAURENCE BINYON. Illustrated. *Demy* 8vo. 18s. *net.*

Hind (A. M.)
A CATALOGUE OF REMBRANDT'S ETCHINGS. Two Vols. Profusely Illustrated. *Wide Royal* 8vo. £1 15s. *net.*

Holdsworth (W. S.)
A HISTORY OF ENGLISH LAW. Nine Volumes. *Demy* 8vo. £1 5s. *net each.*

Hudson (W. H.)
A SHEPHERD'S LIFE. Illustrated. *Demy* 8vo. 10s. 6d. *net.* Also, unillustrated, *Fcap.* 8vo. 3s. 6d. *net.*

Hutton (Edward)
MILAN AND LOMBARDY. THE CITIES OF ROMAGNA AND THE MARCHES. SIENA AND SOUTHERN TUSCANY. VENICE AND VENETIA. THE CITIES OF SPAIN. NAPLES AND SOUTHERN ITALY. Illustrated. *Each,* 8s. 6d. *net.* A WAYFARER IN UNKNOWN TUSCANY. THE CITIES OF UMBRIA. COUNTRY WALKS ABOUT FLORENCE. ROME. FLORENCE AND NORTHERN TUSCANY. Illustrated. *Each,* 7s. 6d. *net.*

Imms (A. D.)
A GENERAL TEXTBOOK OF ENTOMOLOGY. Illustrated. *Royal* 8vo. £1 16s. *net.*

Inge (W. R.), D.D., Dean of St. Paul's
CHRISTIAN MYSTICISM. (The Bampton Lectures of 1899.) *Sixth Edition. Crown* 8vo. 7s. 6d. *net.*

Kipling (Rudyard)
BARRACK-ROOM BALLADS. 233rd *Thousand.*

THE SEVEN SEAS. 172nd *Thousand.*

THE FIVE NATIONS. 138th *Thousand.*

DEPARTMENTAL DITTIES. 111th *Thousand.*

THE YEARS BETWEEN. 95th *Thousand.*
Four Editions of these famous volumes of poems are now published, viz.:—*Crown* 8vo. *Buckram,* 7s. 6d. *net. Fcap.* 8vo. *Cloth,* 6s. *net. Leather,* 7s. 6d. *net.* Service Edition. Two volumes each book. *Square Fcap.* 8vo. 3s. *net* each volume.

A KIPLING ANTHOLOGY—Verse. *Fcap.* 8vo. *Cloth,* 6s. *net. Leather,* 7s. 6d. *net.*

TWENTY POEMS FROM RUDYARD KIPLING. 417th *Thousand. Fcap.* 8vo. 1s. *net.*

A CHOICE OF SONGS. *Second Edition. Fcap.* 8vo. 2s. *net.*

Lamb (Charles and Mary)
THE COMPLETE WORKS. Edited by E. V. LUCAS. A New and Revised Edition in Six Volumes. With Frontispieces. *Fcap.* 8vo. 6s. *net each.*
The volumes are: I. MISCELLANEOUS PROSE. II. ELIA AND THE LAST ESSAYS OF ELIA. III. BOOKS FOR CHILDREN. IV. PLAYS AND POEMS. V. and VI. LETTERS.

SELECTED LETTERS. Chosen and Edited by G. T. CLAPTON. *Fcap.* 8vo. 3s. 6d. *net.*

THE CHARLES LAMB DAY BOOK. Compiled by E. V. LUCAS. *Fcap.* 8vo. 6s. *net.*

Lankester (Sir Ray)
SCIENCE FROM AN EASY CHAIR. SCIENCE FROM AN EASY CHAIR: Second Series. DIVERSIONS OF A NATURALIST. GREAT AND SMALL THINGS. Illustrated. *Crown* 8vo. 7s. 6d. *net.* SECRETS OF EARTH AND SEA. Illustrated. *Crown* 8vo. 8s. 6d. *net.*

Lodge (Sir Oliver)
MAN AND THE UNIVERSE (*Twentieth Edition*). THE SURVIVAL OF MAN (*Seventh Edition*). *Each Crown* 8vo. 7s. 6d. net. RAYMOND (*Twelfth Edition*). *Demy* 8vo. 10s. 6d net. RAYMOND REVISED. *Crown* 8vo. 6s. net. RELATIVITY (*Second Edition*). *Fcap.* 8vo. 1s. net.

Lucas (E. V.)
THE LIFE OF CHARLES LAMB. 2 Vols. £1 1s. net. EDWIN AUSTIN ABBEY, R.A. 2 Vols. £6 6s. net. VERMEER OF DELFT. 10s. 6d. net. A WANDERER IN HOLLAND. A WANDERER IN LONDON. LONDON REVISITED. A WANDERER IN PARIS. A WANDERER IN FLORENCE. A WANDERER IN VENICE. *Each* 10s. 6d. net. A WANDERER AMONG PICTURES. 8s. 6d. net. THE OPEN ROAD. 6s. net. Also, illustrated. 10s. 6d. net, Also, India Paper. *Leather*, 7s. 6d. net. THE FRIENDLY TOWN. FIRESIDE AND SUNSHINE. CHARACTER AND COMEDY. *Each* 6s. net. THE GENTLEST ART. 6s. 6d. net. *And* THE SECOND POST. 6s. net. Also, together in one volume 7s. 6d. net. HER INFINITE VARIETY. GOOD COMPANY. ONE DAY AND ANOTHER. OLD LAMPS FOR NEW. LOITERER'S HARVEST. CLOUD AND SILVER. A BOSWELL OF BAGHDAD. 'TWIXT EAGLE AND DOVE. THE PHANTOM JOURNAL. GIVING AND RECEIVING. LUCK OF THE YEAR. ENCOUNTERS AND DIVERSIONS. ZIGZAGS IN FRANCE. *Each* 6s. net. SPECIALLY SELECTED. URBANITIES. *Each*, illustrated by G. L. STAMPA, 7s. 6d. net. YOU KNOW WHAT PEOPLE ARE. Illustrated by GEORGE MORROW. 5s. net. THE SAME STAR: A Comedy in Three Acts. 3s. 6d. net. THE BRITISH SCHOOL. 6s. net. LITTLE BOOKS ON GREAT MASTERS. *Each* 5s. net. ROVING EAST AND ROVING WEST. 5s. net. INTRODUCING LONDON. 2s. 6d. net. PLAYTIME AND COMPANY. 7s. 6d. net. See also **Dolls' House (The Queen's) and Lamb (Charles)**

Lynd (Robert)
THE MONEY BOX. *Fcap.* 8vo. 6s. net. THE BLUE LION. THE PEAL OF BELLS. *Each Fcap.* 8vo. 3s. 6d. net.

Marie Louise (H.H. Princess)
A CHOICE OF CAROLS. *Fcap.* 4to. 2s. 6d. net.

McDougall (William)
AN INTRODUCTION TO SOCIAL PSYCHOLOGY (*Nineteenth Edition*), 8s. 6d. net. NATIONAL WELFARE AND NATIONAL DECAY. 6s. net. AN OUTLINE OF PSYCHOLOGY. 12s. net. BODY AND MIND (*Fifth Edition*). 12s. 6d. net. ETHICS AND SOME MODERN WORLD PROBLEMS. 7s. 6d. net.

Maeterlinck (Maurice)
THE BLUE BIRD. 6s. net. Also, illustrated by F. CAYLEY ROBINSON. 10s. 6d. net. MARY MAGDALENE. 5s. net. DEATH. 3s. 6d. net. OUR ETERNITY. 6s. net. THE UNKNOWN GUEST. 6s. net. POEMS. 5s. net. THE WRACK OF THE STORM. 6s net. THE MIRACLE OF ST. ANTHONY. 3s. 6d. net. THE BURGOMASTER OF STILEMONDE. 5s. net. THE BETROTHAL. 6s. net. MOUNTAIN PATHS. 6s. net. THE STORY OF TYLTYL. £1 1s. net. THE GREAT SECRET. 7s. 6d. net. THE CLOUD THAT LIFTED and THE POWER OF THE DEAD. 7s. 6d. net.

Masefield (John)
ON THE SPANISH MAIN. 8s. 6d. net. A SAILOR'S GARLAND. 6s. net. SEA LIFE IN NELSON'S TIME. 5s. net.

Methuen (Sir A.)
AN ANTHOLOGY OF MODERN VERSE. 107*th Thousand*.
SHAKESPEARE TO HARDY: An Anthology of English Lyrics. 15*th Thousand*. *Each Fcap.* 8vo. *Cloth*, 6s. net. *Leather*, 7s. 6d. net.

Milne (A. A.)
NOT THAT IT MATTERS. IF I MAY. *Each* 3s. 6d. net. WHEN WE WERE VERY YOUNG. Illustrated by E. H. SHEPARD *Twelfth Edition*. 102*nd Thousand*. 7s. 6d. net. *Leather*, 10s. 6d. net. FOR THE LUNCHEON INTERVAL: CRICKET AND OTHER VERSES. 1s. 6d. net.

Milne (A. A.) and Fraser-Simson (H.)
FOURTEEN SONGS FROM "WHEN WE WERE VERY YOUNG." Words by A. A. Milne. Music by H. Fraser-Simson. *Sixth Edition*. *Royal* 4to. 7s. 6d. net. THE KING'S BREAKFAST. *Crown* 4to. 3s. 6d. net.

Montague (C. E.)
DRAMATIC VALUES. *Crown* 8vo. 7s. 6d. net.

Newman (Tom)
HOW TO PLAY BILLIARDS. Illustrated. *Crown* 8vo. 8s. 6d. net. BILLIARD DO'S AND DON'TS. 2s. 6d. net.

Oman (Sir Charles)
A HISTORY OF THE ART OF WAR IN THE MIDDLE AGES, A.D. 378–1485. *Second Edition*, Revised and Enlarged. 2 Vols. Illustrated. *Demy 8vo.* £1 16*s. net.*

Oxenham (John)
BEES IN AMBER. *Small Pott 8vo.* 2*s. net.* ALL'S WELL. THE KING'S HIGHWAY. THE VISION SPLENDID. THE FIERY CROSS. HIGH ALTARS. HEARTS COURAGEOUS. ALL CLEAR! *Each Small Pott 8vo. Paper*, 1*s.* 3*d. net. Cloth*, 2*s. net.* WINDS OF THE DAWN. 2*s. net.*

Perry (W. J.)
THE ORIGIN OF MAGIC AND RELIGION. THE GROWTH OF CIVILIZATION. *Each* 6*s. net.* THE CHILDREN OF THE SUN. 18*s net.*

Petrie (Sir Flinders)
A HISTORY OF EGYPT. In 6 Volumes.

Vol. I. FROM THE IST TO THE XVITH DYNASTY. *Eleventh Edition, Revised.* 12*s. net.*

Vol. II. THE XVIITH AND XVIIITH DYNASTIES. *Seventh Edition, Revised.* 9*s. net.*

Vol. III. XIXTH TO XXXTH DYNASTIES. *Third Edition.* 12*s. net.*

Vol. IV. EGYPT UNDER THE PTOLEMAIC DYNASTY. J. P. MAHAFFY. *Second Edition.* 9*s. net.*

Vol. V. EGYPT UNDER ROMAN RULE. J. G. MILNE. *Third Edition, Revised.* 12*s. net.*

Vol. VI. EGYPT IN THE MIDDLE AGES. STANLEY LANE POOLE. *Fourth Edition.* 10*s. net.*

leigh (Sir Walter)
THE LETTERS OF SIR WALTER RALEIGH. Edited by LADY RALEIGH. Two Vols. Illustrated. *Demy 8vo.* £1 10*s. net.*

s-Oxley (L.)
OXFORD RENOWNED. Illustrated. *Demy 8vo.* 18*s. net.*

(Adam)
THE WEALTH OF NATIONS. Edited by EDWIN CANNAN. 2 Vols. *Demy 8vo.* £1 5*s. net.*

Smith (C. Fox)
SAILOR TOWN DAYS. SEA SONGS AND BALLADS. A BOOK OF FAMOUS SHIPS. SHIP ALLEY. FULL SAIL. *Each*, illustrated, 6*s. net.* THE RETURN OF THE "CUTTY SARK." Illustrated. 3*s.* 6*d. net.*

Sommerfeld (Arnold)
ATOMIC STRUCTURE AND SPECTRAL LINES. *Demy 8vo.* £1 12*s. net.*

Stevens (F. E.)
THE NEW FOREST BEAUTIFUL. Illustrated. *Crown 8vo.* 8*s.* 6*d. net.*

Stevenson (R. L.)
THE LETTERS. Edited by Sir SIDNEY COLVIN. 4 Vols. *Fcap. 8vo. Each* 6*s. net.*

Stratton (F. J. M.)
ASTRONOMICAL PHYSICS. *Demy 8vo.* 15*s. net.*

Surtees (R. S.)
HANDLEY CROSS. MR. SPONGE'S SPORTING TOUR. ASK MAMMA. MR. FACEY ROMFORD'S HOUNDS. PLAIN OR RINGLETS? HILLINGDON HALL. *Each*, illustrated, 7*s.* 6*d. net.* JORROCKS'S JAUNTS AND JOLLITIES. HAWBUCK GRANGE. *Each*, illustrated, 6*s. net.*

Thomson (J. Arthur)
WHAT IS MAN? 6*s.* 6*d. net.* SCIENCE AND RELIGION. 7*s.* 6*d. net.*

Tilden (W. T.)
THE ART OF LAWN TENNIS. SINGLES AND DOUBLES. *Each*, illustrated, 6*s. net.* THE COMMON SENSE OF LAWN TENNIS. Illustrated. 5*s. net.*

Tileston (Mary W.)
DAILY STRENGTH FOR DAILY NEEDS. *31st Edition.* 3*s.* 6*d. net. India Paper, Leather*, 6*s. net.*

Underhill (Evelyn)
MYSTICISM (*Tenth Edition*). 15*s. net.* THE LIFE OF THE SPIRIT AND THE LIFE OF TO-DAY (*Sixth Edition*). 7*s.* 6*d. net.*

Vardon (Harry)
HOW TO PLAY GOLF. Illustrated. *18th Edition. Crown 8vo.* 5*s. net.*

Waterhouse (Elizabeth)
A LITTLE BOOK OF LIFE AND DEATH. *22nd Edition. Small Pott 8vo.* 2*s.* 6*d. net.*

Wilde (Oscar).
THE WORKS. In 16 Vols. *Each* 6s. 6d. *net*.

I. LORD ARTHUR SAVILE'S CRIME AND THE PORTRAIT OF MR. W. H. II. THE DUCHESS OF PADUA. III. POEMS. IV. LADY WINDERMERE'S FAN. V. A WOMAN OF NO IMPORTANCE. VI. AN IDEAL HUSBAND. VII. THE IMPORTANCE OF BEING EARNEST. VIII. A HOUSE OF POMEGRANATES. IX. INTENTIONS. X. DE PROFUNDIS AND PRISON LETTERS. XI. ESSAYS. XII. SALOME, A FLORENTINE TRAGEDY, and LA SAINTE COURTISANE. XIII. A CRITIC IN PALL MALL. XIV. SELECTED PROSE OF OSCAR WILDE. XV. ART AND DECORATION. XVI. FOR LOVE OF THE KING. 5s. *net*.

PART II. A SELECTION OF SERIES

The Antiquary's Books
Each, illustrated, *Demy* 8*vo*. 10s. 6d. *net*. A series of volumes dealing with various branches of English Antiquities, comprehensive and popular, as well as accurate and scholarly.

The Arden Shakespeare
Edited by W. J. CRAIG and R. H. CASE. *Each*, *wide Demy* 8*vo*. 6s. *net*.
The Ideal Library Edition, in single plays, each edited with a full Introduction, Textual Notes and a Commentary at the foot of the page. Now complete in 39 Vols.

Classics of Art
Edited by J. H. W. LAING. *Each*, profusely illustrated, *wide Royal* 8*vo*. 15s. *net to* £3 3s. *net*.
A Library of Art dealing with Great Artists and with branches of Art.

The "Complete" Series
Demy 8*vo*. Fully illustrated.
AIRMAN. 16s. *net*. AMATEUR BOXER. 10s. 6d. *net*. ATHLETIC TRAINER. 10s. 6d. *net*. BILLIARD PLAYER. 10s. 6d. *net*. COOK. 10s. 6d. *net*. FOXHUNTER. 16s. *net*. GOLFER. 12s. 6d. *net*. HOCKEY PLAYER. 10s. 6d. *net*. HORSEMAN. 15s *net*. JUJITSUAN (*Cr.* 8*vo*.). 5s. *net*. LAWN TENNIS PLAYER. 12s. 6d. *net*. MOTORIST. 10s. 6d. *net*. MOUNTAINEER. 18s. *net*. OARSMAN. 12s. 6d. *net*. PHOTOGRAPHER. 12s. 6d. *net*. RUGBY FOOTBALLER, ON THE NEW ZEALAND SYSTEM. 12s. 6d. *net*. SHOT. 16s. *net*. SWIMMER. 10s. 6d. *net*. YACHTSMAN. 15s. *net*.

The Connoisseur's Library
With numerous Illustrations. Wide Royal 8*vo*. £1 11s. 6d. *net each vol*.
EUROPEAN ENAMELS. FINE BOOKS. GLASS. GOLDSMITHS' AND SILVERSMITHS' WORK. IVORIES. JEWELLERY. MEZZOTINTS. PORCELAIN. SEALS.

The Do's and Dont's Series
Fcap. 8*vo*. 2s. 6d. *net each*.
This series, although only in its infancy, is already famous. In due course it will comprise clear, crisp, informative volumes on all the activities of life.
Write for full list

The Library of Devotion
Handy editions of the great Devotional books, well edited. *Small Pott* 8*vo*. 3s. *net and* 3s. 6d. *net*.

Little Books on Art
Well Illustrated. *Demy* 16*mo*. *Each* 5s. *net*.

Modern Masterpieces
Fcap. 8*vo*. 3s. 6d. *each volume*.
Pocketable Editions of Works by A. A. MILNE, JOSEPH CONRAD, ARNOLD BENNETT, G. K. CHESTERTON, E. V. LUCAS, HILAIRE BELLOC, W. H. HUDSON and ROBERT LYND.

Sport Series
Mostly Illustrated. *Fcap*. 8*vo*. 2s. *net to* 5s. *net each*.
Handy books on all branches of sport by experts.

Methuen's Half-Crown Library
Crown 8vo and Fcap. 8vo.

Methuen's Two Shilling Library
Fcap. 8vo.

Two series of cheap editions of popular books.

Write for complete lists

The Westminster Commentaries
Demy 8vo. 8s. 6d. net to 16s. net.
Edited by W. LOCK, D.D. The object of these commentaries is primarily to interpret the author's meaning to the present generation, taking the English text in the Revised Version as their basis.

THE LITTLE GUIDES

Small Pott 8vo. Illustrated and with Maps

4s. net mostly

THE 62 VOLUMES IN THE SERIES ARE:—

BEDFORDSHIRE AND HUNTINGDONSHIRE
BERKSHIRE
BRITTANY
BUCKINGHAMSHIRE
CAMBRIDGE AND COLLEGES
CAMBRIDGESHIRE
CATHEDRAL CITIES OF ENGLAND AND WALES 6s. net
CHANNEL ISLANDS 5s. net
CHESHIRE 5s. net
CORNWALL
CUMBERLAND AND WESTMORLAND 6s. net
DERBYSHIRE
DEVON
DORSET 5s. 6d. net
DURHAM
ENGLISH LAKES 6s. net
ESSEX
GLOUCESTERSHIRE
GRAY'S INN AND LINCOLN'S INN 6s. net
HAMPSHIRE
HEREFORDSHIRE 4s. 6d. net
HERTFORDSHIRE
ISLE OF MAN 6s. net
ISLE OF WIGHT
KENT 5s. net
KERRY
LANCASHIRE 6s. net
LEICESTERSHIRE AND RUTLAND 5s. net
LINCOLNSHIRE 6s. net
LONDON
MALVERN COUNTRY
MIDDLESEX
MONMOUTHSHIRE
NORFOLK 5s. net
NORMANDY 5s. net
NORTHAMPTONSHIRE
NORTHUMBERLAND 7s. 6d. net
NORTH WALES 6s. net
NOTTINGHAMSHIRE
OXFORD AND COLLEGES
OXFORDSHIRE
ROME 5s. net
ST. PAUL'S CATHEDRAL
SHAKESPEARE'S COUNTRY
SHROPSHIRE
SICILY
SNOWDONIA 6s. net
SOMERSET
SOUTH WALES
STAFFORDSHIRE 5s. net
SUFFOLK
SURREY
SUSSEX
TEMPLE
WARWICKSHIRE 5s. net
WESTMINSTER ABBEY
WILTSHIRE 6s. net
WORCESTERSHIRE 6s. net
YORKSHIRE EAST RIDING 5s. net
YORKSHIRE NORTH RIDING
YORKSHIRE WEST RIDING 7s. 6d. net
YORK 6s. net

METHUEN & CO. LTD., 36 ESSEX STREET, LONDON, W.C

A1186